University of Alberta

THE ROLE OF SILICA DEPLETION IN THE EUTROPHICATION OF LAC LA BICHE, ALBERTA

by

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Abstract

Eutrophication of aquatic systems can induce silica (Si) depletion through enhanced production and sedimentation of diatoms. This may shift the phytoplankton assemblage to include increasing proportions of non-siliceous taxa such as potentially nuisance Cyanobacteria. I examined the role of Si depletion in the eutrophication of Lac la Biche, a large lake in northern Alberta. Paleolimnological analyses indicate that while Lac la Biche has undergone eutrophication since the mid-20th century, there is no evidence for either Si depletion or Si mediated shifts in the relative proportion of diatoms and Cyanobacteria. However, I show through nutrient amendment experiments that Si depletion can be induced seasonally under specific nutrient regimes. Further, Si amendment significantly increased the proportion of diatoms relative to Cyanobacteria. I conclude that with ongoing eutrophication and anticipated declines in Si loading to aquatic systems associated with drought and climate warming, Si depletion may become increasingly important in structuring phytoplankton communites.

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Chapter 1: General Introduction

Eutrophication is a widespread form of limnological pollution resulting from increased loading of phosphorus (P) and nitrogen (N). Increased productivity and changes in phytoplankton assemblages associated with eutrophication are responsible for a number of deleterious changes including abundant macrophyte growth, increased frequency and duration of algal blooms, low dissolved oxygen concentrations, and a general decline in water quality (Carpenter et al. 1998). Eutrophication may eventually result in lake instability and a loss of biodiversity (Margalef 1968).

The ecological consequences of eutrophication may be further complicated by indirect effects of nutrient loading on dissolved silicate (Si) concentrations. Si is an essential nutrient for siliceous algae such as diatoms (Bacillariophyceae). Diatoms are widespread, abundant and are a high quality food source for grazers. Consequently they play an important role in the structuring of aquatic food webs (Round et al. 1990). Because they are enclosed in a silicified wall or frustule, their production is dependent on an adequate supply of Si.

Eutrophication can induce Si depletion in a process known as biologically mediated silica depletion (BMSD) (Schelske and Stoermer 1971, Schelske et al. 1986, Schelske et al. 2006). BMSD occurs when increased nutrient loading stimulates enhanced production and sedimentation of diatoms, and a portion of their siliceous frustules become permanently sequestered in the sediment. This loss of Si to the sediment, coupled with more efficient cycling of sediment P relative to Si, results in lower Si concentrations in the water column and may lead to seasonal or year round Si limitation (Schelske and Stoermer 1971, Schelske et al. 1986, Schelske et al. 2006). Because reduced Si concentrations may decrease the proportion of diatoms relative to non-siliceous algae, including potentially nuisance forms such as Cyanobacteria, (Schelske and Stoermer 1971, Officer and Ryther 1980, Egge and Aksnes 1992, Horn and Uhlmann 1995), BMSD may exacerbate the harmful consequences of eutrophication, altering phytoplankton community structure (Kilham 1971, Officer and Ryther 1980, Conley et al. 1993, Schelske 1999, Rocha et al. 2002), food web dynamics (Turner et al. 1998, Humborg et al. 2000), and nutrient cycling processes

(Smetacek 1985, Conley et al. 1993).

In freshwater, BMSD has been best described in large, naturally oligotrophic lakes with long water residence times such as the Laurentian Great Lakes (Conley et al. 1993, Schelske 1999, Conley and Schelske 2001). However, there is evidence that BMSD may operate in a wide variety of geographically and ecologically disparate systems. Observational data from contemporary data sets have linked eutrophication events with changes in the seasonal decline of Si concentrations in oligotrophic lakes in arctic Canada (Welch et al. 1989) and the UK (Talling and Heaney 1988), as well as in coastal marine systems in North America and Europe (Conley et al. 1993, Turner and Rabalais 1994, Humborg et al. 2000). Additionally, long term Si depletion that resulted in epilimnetic Si limitation has been inferred from sediment cores collected in Africa (Verschuren et al. 1998) and Europe (Schelske et al. 1987), and in both cases Si limited diatom production was coincident with increasing Cyanobacteria abundance.

Although BMSD is apparently ubiquitous, an examination of the role of silica depletion in eutrophication has not been conducted in boreal North America, where short growing seasons may limit the ability of diatom blooms to deplete Si concentrations to potentially limiting concentrations. BMSD has also not yet been reported in Western Canada, though eutrophication is common in the region (Schindler and Donahue 2006). Finally, BMSD has not been studied in eutrophic or hypereutrophic lakes, and it remains unclear whether these systems, which may be less sensitive to increased N and P input, will exhibit BMSD as has been shown previously in oligotrophic systems.

I examined the role of Si depletion in the eutrophication of Lac la Biche, a large, shallow, hypereutrophic (total phosphorus (TP) = 40-330 $\mu g\ L^{-1}$, chlorophyll *a* (chl *a*) = 10-180 $\mu g\ L^{-1}$) boreal lake in northern Alberta, Canada. Complaints from local residents suggest that there have been recent declines in water quality. The symptoms cited are those most often attributed to eutrophication, including increasing frequency and duration of algal blooms, taste and odour problems, and periodic fish kills (Carpenter et al. 1998). Land clearing, agricultural run-off, and cottage septic waste are likely all non-point sources of nutrient loading to Lac la Biche. Point sources include primary treated sewage effluent from the town of Lac la Biche that has

been emptied directly or indirectly into the lake since 1951. Water chemistry survey data collected in 2003 indicate that Si concentrations that approach or fall below potentially limiting concentrations of < 0.5 mg L^{-1} (Schelske 1999) occur transiently in some bays of Lac la Biche in the late spring (0.64 mg L^{-1}) and mid to late summer (0.17 mg L^{-1}), particularly in the basin that receives sewage effluent (Schindler et al., unpublished data).

Because there are no long term water quality data for Lac la Biche, I used several independent paleolimnological techniques to infer historical changes in nutrient loading, primary productivity, biogenic Si (BSi) deposition to lake sediments and phytoplankton community structure. I additionally conducted a nutrient amendment experiment in mesocosms deployed in Lac la Biche in order to test BMSD as a possible mechanism for Si depletion in the lake, and to determine its effect on seasonal phytoplankton succession. The objectives of this study were: 1) to determine if historical Si depletion may have been a factor in declining water quality by contributing to a shift from diatom to Cyanobacteria dominated phytoplankton assemblages; 2) to determine if potentially limiting Si concentrations could be induced by N and P addition in a northern, hypereutrophic lake; and 3) to investigate the consequence of reduced Si concentrations on phytoplankton biomass and community structure.

The objectives are addressed in the following two chapters. In the first chapter, I use total N (TN) and total P (TP) concentrations, N stable isotopes, BSi and fossil pigments concentrations in sediment cores collected from the two major basins of Lac la Biche to examine changes in nutrient loading and the phytoplankton community as a result of regional land-use changes over time. In the second chapter, I examine changes in Si concentrations as well as phytoplankton biomass and community composition in response to nutrient amendment experiments conducted throughout the summer of 2004. The results of this study are intended to inform the Lac la Biche steering committee on the critical need for managing nutrient loading from the watershed. In addition, it is my intention that it will supplement current understanding of the mechanisms by which phytoplankton communities are structured in boreal lakes.

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Chapter 2: Paleolimnological analysis of eutrophication and silica mediated changes in phytoplankton community composition in Lac la Biche, Alberta

Introduction

Eutrophication remains a widespread form of limnological pollution despite more than 40 years of scientific research on its prevention and management (Hall and Smol 1999, Schindler 2006). Eutrophication occurs through increased loading of phosphorus (P) and nitrogen (N) and is commonly accompanied by abundant macrophyte growth, increased frequency and duration of algal blooms, low dissolved oxygen concentrations, and a general decline in water quality (Carpenter et al. 1998). Changes occurring at the southern boundary of Alberta's boreal region such as cottage development and the conversion of forest to pasture and cropland and may hasten eutrophication and water quality decline (Neufeld 2005).

Lac la Biche is a large, hypereutrophic (total P (TP) = 40-330 $\mu g\ L^{-1}$, chlorophyll *a* (chl *a*) = 10-180 $\mu g\ L^{-1}$), boreal lake in northern Alberta, Canada. Anthropogenic impact likely began with European settlement in 1798. Early regional surveyors reported overexploitation of fish resources as early as the late 19th century. Land clearing, agricultural run-off and septic tank waste are likely historical and current non-point sources of nutrient loading. With the development of the first modern waste water treatment plant in 1951, primary treated sewage effluent from the town of Lac la Biche emptied directly into the lake. Though sewage outflow was diverted to nearby Field Lake in 1983, sewage effluent continues to enter Lac la Biche through Red Deer Brook which drains Field Lake.

Complaints from local residents suggest that there have been recent declines in water quality. The symptoms cited include those most often attributed to eutrophication, including increasing frequency and duration of algal blooms, taste and odour problems and periodic fish kills. In addition, water chemistry data from 2003 indicate that dissolved silica (Si) concentrations that approach or fall below potentially limiting concentrations of < 0.5 mg L^{-1} (Schelske 1999) occur transiently in Lac la Biche in the late spring (0.64 mg L^{-1}) and mid to late summer (0.17 mg L^{-1}) in the basin that receives sewage effluent (Schindler et al., unpublished data).

Eutrophication can induce Si depletion in a process known as biologically mediated silica depletion (BMSD) (Schelske et al. 2006). BMSD occurs when increased nutrient loading stimulates enhanced production and sedimentation of diatoms, and a portion of their siliceous frustules become permanently sequestered in the sediment. This loss of Si to the sediment, coupled with more efficient cycling of sediment P relative to Si, results in lower Si concentrations in the water column and may lead to seasonal or year round Si limitation (Schelske and Stoermer 1971, Schelske et al. 1986, Schelske et al. 2006). Because reduced Si concentrations may decrease the proportion of diatoms relative to non-siliceous algae, including potentially nuisance forms such as Cyanobacteria (Schelske and Stoermer 1971, Officer and Ryther 1980, Egge and Aksnes 1992, Horn and Uhlmann 1995), BMSD may exacerbate the deleterious consequences of eutrophication.

To determine if Lac la Biche has undergone eutrophication and if Si depletion has contributed to water quality decline, a number of independent paleolimnological techniques were used to infer historical changes in nutrient loading, primary productivity and phytoplankton community structure. I used total P (TP) concentrations, total N (TN):TP ratios and N stable isotope ratios to infer historical changes in nutrient loading (Heaton 1986, Brenner et al. 1999, Boyle 2001, Talbot 2001, Leavitt et al. 2006). Fossil chl *a* concentrations were used as proxies for paleoproductivity (Hodell and Schelske 1998, Brenner et al. 1999, Leavitt and Hodgson 2001). Biogenic silica (BSi) concentrations were used to infer historical production of siliceous algae, to identify periods of Si limitation in the lake and to examine the possibility that BMSD has occurred in Lac la Biche (Schelske 1999, Conley and Schelske 2001). Concentrations of fossil pigments indicative of Cyanobacteria (echinenone and canthaxanthin) as well as green algae and Cyanobacteria (lutein-zeaxanthin) were used to infer changes in the paleoproductivity of those specific taxa (Engstrom et al. 1985, Hall et al. 1999, Leavitt and Hodgson 2001).

The objectives of this study were: 1) to determine if historical changes in nutrient loading, primary productivity and phytoplankton community structure correlate with anthropogenic activities in Lac la Biche; and 2) to determine if Si

depletion may have contributed to declining water quality by causing a shift from diatom to Cyanobacteria dominated assemblages.

Methods

Study Area

Lac la Biche is a large, shallow lake (mean depth = 8.4 m, maximum depth = 21.3 m) with an area of 234 km^2 and a catchment area of 4040 km^2 (Mitchell and Prepas 1990). It is located at 54° 52' N latitude, 112° 05' W longitude in the mid-boreal mixedwood ecoregion (Strong 1992) in north-central Alberta. The lake is comprised of two major basins (Figure 2.1). The town of Lac la Biche and site of sewage inflow are located on the south side of the east basin. Both basins are affected by cottage development and agriculture, with agricultural sites concentrated on the south and west sides of the lake.

Sediment coring

Sediment cores were obtained from locations D1 and D3, the deepest points in the east and west basin (hereafter referred to as basins D1 and D3 respectively). The cores were collected in February 2003 using a Glew gravity corer. A total of 4 cores, 0.5 to 1 m in length, were taken at each site. They were sectioned at either 0.5 cm or 1 cm intervals, frozen and freeze-dried.

Analysis

Sediments were dated using ^{210}Pb analysis by gamma spectrometry at the University of Ottawa, Ontario, Canada. Sediment age and mass sedimentation rate ($g\ cm^{-2}\ yr^{-1}$) were calculated using the constant rate of supply (CRS) model (Appleby 2001). Loss on ignition (500°C for 2 hours), TP and TN were analyzed according to standard methods at the Limnological Services Unit at the University of Alberta, Edmonton, Canada. TN was analyzed with a CHN Elemental Analyzer and TP was analyzed colourimetrically with a spectrophotometer. TN and TP concentrations were used to calculate nutrient ratios (by weight) for each sediment interval.

Sediments for BSi analysis were pre-digested according to Mortloch and Froelich (1989) and analyzed using the wet alkaline method of Conley and Schelske (2001). Briefly, 30 mg of sediment was pre-digested with 10% H_2O_2 for 30 minutes followed by 1 N HCl for an additional 30 minutes to disaggregate the sediment. Subsequently, 20 mL of deionized water was added and the samples were centrifuged at 4300 *g* for 5 minutes. The supernatant was decanted and samples were dried overnight at 60°C. Samples were subsequently incubated with 40 mL of 1% Na_2CO_3 in a shaker bath at 85° C and 100 rpm. Supernatant was sub-sampled after 3, 4 and 5 hours and analyzed for molybdate-reactive silicon using a Technicon AutoAnalyzer II according to standard methods at the Limnological Services Unit at the University of Alberta. Si concentrations at each of the three sampling periods were averaged to infer BSi concentrations at zero time.

N stable isotope ratios were determined by analyzing about 3 mg of sediment with a continuous flow IRMS using a GV Instruments IsoPrime mass spectrometer with a EuroVector EuroEA3028-HT elemental analyzer. Analysis was performed at the Limnological Services Unit, University of Alberta. All nitrogen isotopic results are expressed in conventional δ notation relative to air as $\delta^{15}N = (R_{sample}/R_{standard}-1) \times 1000$ where R is the measured $^{15}N/^{14}N$ ratio.

Fossil pigment data were obtained from Dr. Rolf Vinebrooke at the University of Alberta, Edmonton, Canada. Sedimentary pigments were extracted, filtered and dried under N_2 gas and were quantified using a Hewlett-Packard model 1100 high-performance liquid chromotograph (HPLC) following the reversed-phase procedure of Mantoura and Llewellyn (1983) as modified by Leavitt et al. (1989, 1999). Pigments analyzed included chl *a*, and the carotenoid pigments echinenone, lutein-zeaxanthin and canthaxanthin.

Data obtained from the analysis of the top 5 cm of the cores (ca. 1999 to 2003) were excluded from interpretation due the probability that these surface muds contained siliceous remains and organic matter still subject to dissolution or diagenetic processes before permanent burial (Conley and Schelske 1989, Schelske and Hodell 1991, Leavitt 1993, Leavitt and Findlay 1994).

Results

Chronology

^{210}Pb activity declined in a non-monotonic manner with depth, suggesting the CRS model applied to determine sediment age is appropriate (Figure 2.2). In the D3 core, there was increase in ^{210}Pb activity with decreasing core depth until 10 cm, above which ^{210}Pb activity declined. The surface decline in ^{210}Pb activity may be due to decreased ^{210}Pb inputs from the surrounding catchment as a result of decreased surface water flow with recent drought. Though this anomaly limits the ability of the CRS model to accurately ascertain specific dates in the upper section of the D3 core, the use of the ^{210}Pb dating profile is appropriate to identify long-term trends as was required for this study. Because ^{210}Pb dating analysis does not predate European contact in the region, pre- and post-European settlement conditions cannot be compared. However, changes in the trophic history of Lac la Biche can be ascertained over the past 130 years when the impacts of population growth, land clearing, agriculture and sewage effluent have become progressively more intensive.

Nutrient loading

Sediment TP concentration and TP flux increased over time in both basins of Lac la Biche (Figure 2.3). In D1, TP concentrations nearly doubled, from approximately 1.4 mg g^{-1} in the late 19th century to 2.7 mg g^{-1} in recent sediment. TP flux increased more than 7 fold, from 0.015 to 0.11 mg cm^{-2} yr^{-1}, over the same period. Increases in both concentration and flux of TP began ca. 1950 in D1. In D3, the TP concentrations have doubled, from 1.2 mg g^{-1} to 2.4 mg g^{-1} and TP flux increased approximately 10 fold, from 0.007 to 0.078 mg cm^{-1} yr^{-1}. The rate of increase of both TP flux and TP concentration in D3 appears to have accelerated after 1975.

TN:TP ratios declined in both D1 and D3, although the decline began near 1950 in D1 and 1975 in D3 (Figure 2.4). Both basins have similar background TN:TP ratios near 15 (by weight) and more recent ratios of about 8.

δ^{15}N signatures differ substantially between basins (Figure 2.5). In D1, which receives sewage input, δ^{15}N increased from approximately 4.8‰ to 5.7‰ between ca. 1960 and 1980. After 1980, δ^{15}N declined to approximately 5.0‰. The δ^{15}N

signature of D3 has declined steadily from approximately 3.7‰ in 1886 to 2.1‰ in recent sediments.

Changes in Paleoproductivity

Chl *a* concentrations in sediments from D1 have doubled since ca. 1950, increasing from approximately 15 to 30 $\mu g\ g^{-1}$OM. They did not increase substantially in D3 (Figure 2.6). However, chl *a* flux increased in both D1 and D3 sediment cores after about 1950. In D3, flux rates increased more than 4 times from pre-1950 values of approximately 0.7 to greater than 3 $\mu g\ cm^{-2}\ yr^{-1}$. The relative increase in chl *a* flux rates in D1 was much greater, increasing approximately 40 fold from about 0.005 to 0.2 $\mu g\ cm^{-2}\ yr^{-1}$ since 1950

Changes in Algal Community Structure

BSi, a proxy for the productivity of siliceous taxa such as diatoms, chrysophytes, and freshwater sponges, increased in both D1 and D3 over time (Figure 2.7). In D1, BSi concentrations increased from approximately 27 mg g^{-1} prior to 1950 to 45 mg g^{-1} in 2000. In D3, there was no trend in BSi concentrations due to high background variability. However, BSi flux consistently increased in both cores. In D1, BSi flux increased more than 6 fold, from 0.3 mg $cm^{-2}\ yr^{-1}$ prior to 1950 to approximately 1.9 mg $cm^{-2}\ yr^{-1}$ in 2000. BSi flux in D3 showed two periods of increase. Prior to ca. 1915, BSi flux was approximately 0.3 mg $cm^{-2}\ yr^{-1}$. Flux subsequently increased to 2.0 mg $cm^{-2}\ yr^{-1}$ by ca. 1950. It increased again to reach approximately 3 mg $cm^{-2}\ yr^{-1}$ by 2000. Overall, there was about a 13 fold increase in BSi flux in D3.

Fossil pigments indicative of Cyanobacteria (echinenone and canthaxanthin) and pigments associated with both green algae and Cyanobacteria (lutein-zeaxanthin) were present throughout the cores, suggesting that potentially nuisance algae have been present in Lac la Biche throughout the last 130 years (Figure 2.8). However, the abundance of these taxa increased in the last half of the 20th century. Despite high background variability, there were increasing trends in canthaxanthin and lutein-zeaxanthin concentrations in both basins, suggesting that Cyanobacteria and possibly green algae increased in biomass in the last 50 years. Larger increases in the flux rates

of pigments occurred in both basins since about 1950. Flux rates of canthaxanthin, echinenone, and lutein-zeaxanthin increased 8 to 10 fold over background in basin D1 and 2 to 3 fold in D3.

Discussion

History of water quality changes

Consistent with Mitchell and Prepas (1990) and inferences derived from the analysis of Lac la Biche diatom fossils (Schindler et al., unpublished data), I conclude that Lac la Biche was historically eutrophic. However, I find evidence of cultural eutrophication in the last half of the 20th century as inferred from increases in TP, declining TN:TP ratios, increasing $\delta^{15}N$ until ca. 1980 (in the D1 core) and increases in fossil pigments and BSi in sediment cores. Declining TN:TP ratios, along with increasing TP concentration and flux are consistent with anthropogenic nutrient input both from agricultural run-off and sewage effluent, which are high in P relative to N (Schelske et al. 1985, Cooke and Prepas 1998, Havlin et al. 2005).

Paleolimnological studies often favour the use of diatom-TP transfer functions as opposed to sediment TP concentrations an indicator of historic trophic state (Boyle 2001). This is because diatoms respond quickly to environmental change, individual species have a particular optimum range and tolerance of nutrient supply rates and ratios, and the large number of taxa provide data redundancy that can be used as internal checks to increase the confidence of inferences (Hall and Smol 1999). Conversely, P is susceptible to sediment loss or enrichment with changing redox conditions and stratigraphic variations in P may vary with iron content (Boyle 2001). However, the construction of diatom-TP transfer functions is time intensive, and, if interpreted cautiously, sediment P is useful in reconstructing historical changes in trophic status (Boyle 2001). In the case of Lac la Biche, where trends in nutrient concentrations are large and there is temporal correlation between anthropogenic activities and changes in sediment TP concentration and TN:TP ratios, I conclude that sediment TP concentrations have been used accurately to infer changes in trophic status.

I suggest that the $\delta^{15}N$ signatures in cores D1 and D3 largely represent changes

in the source of dissolved inorganic nitrogen as opposed to changes in productivity or biogeochemical processes as has been shown elsewhere (Hodell and Schelske 1998, Brenner et al. 1999). This is primarily because decreasing trends in $\delta^{15}N$ in D1 after 1980 and in D3 do not track increases in productivity proxies such as diatom abundance (Schindler et al., unpublished data) or concentration and flux rates of BSi and chl *a*. Further, there is temporal correlation between the increase in $\delta^{15}N$ and the loading of sewage effluent to D1 since 1950. Sewage effluent is typically enriched in $\delta^{15}N$ from 10 – 20‰ (Heaton 1986) but may be enriched greater than 30‰ where microbial denitrification has occurred (Savage et al. 2004). My results confirm those of Leavitt et al. (2006), who reported enriched $\delta^{15}N$ in lake sediments as a result of the release of sewage effluent, and that increases in $\delta^{15}N$ were correlated with increasing algal productivity inferred from fossil pigments.

The decline in $\delta^{15}N$ over time in D3 may be due to increasing contribution of N from N_2 fixation, which has a $\delta^{15}N$ signature near 0‰ (Talbot 2001). This is consistent with increasing trends in Lac la Biche fossil Cyanobacteria pigments in the last half of the 20th century. Further, while $\delta^{15}N$ increases with increased productivity in oligotrophic systems (Hodell and Schelske 1998), this relationship breaks down in hypereutrophic systems due to the presence of nitrogen fixers (Gu et al. 1996, Brenner et al. 1999). Declining $\delta^{15}N$ throughout the last century may also reflect increased atmospheric nitrogen deposition as a result of NO_x emission (Husar 1986, Bennett 1986). While atmospheric deposition and N_2 fixation have likely affected D1 and D3 similarly, in D1 this signal was probably overwhelmed by the loading of sewage effluent until 1980. The decline in $\delta^{15}N$ in the last two decades in basin D1 may reflect an increase in nitrogen fixation which overwhelmed the signal from sewage effluent. In addition, declining regional surface water flows (Schindler and Donahue 2006) could have decreased the input of sewage effluent into basin D1 via Red Deer Brook. This would additionally account for stable TN:TP ratios since ca. 1980 in D1 while TN:TP ratios declined in D3.

I conclude that changes in water quality of Lac la Biche have occurred since the mid 20th century. Consistent with lake survey data collected from 2003-2005 (Schindler et al., unpublished data), my data suggest that basin D1 has been most

affected by anthropogenic eutrophication, and D3 has been affected to a lesser extent. Additionally, changes in TP, TN:TP ratios and $\delta^{15}N$ in D1 coincide with the development of the first modern waste water treatment plant in the area, and thus with the beginning of direct loading of sewage effluent to that basin. The differing responses of the two major basins allow us to compare the effects of activities that impact both basins, such as agriculture, land clearing and cottage development with those that directly affect only D1, such as sewage effluent. I suggest the rise in nutrient loading in D3 after ca. 1975 and more recent increases in productivity in that basin are the result of land clearing, agriculture and cottage development which has increased with improved road access. In contrast, increased nutrient flux in D1, which began after 1950, is additionally influenced by sewage effluent.

Silica depletion and silica mediated changes in phytoplankton community structure

In freshwater, BMSD has been best documented in large, naturally oligotrophic lakes with long residence times such as the Laurentian Great Lakes (Conley et al. 1993, Schelske 1999, Conley and Schelske 2001). However, BMSD may operate in a wide variety of geographically and ecologically disparate systems, such as lakes in Europe (Lund 1972, Schelske et al.1987, Talling and Heaney 1998), Africa (Verschuren et al. 1998), arctic Canada (Welch et al. 1989), as well as in coastal and marine systems in North America and Europe (Conley et al. 1993, Turner and Rabalais 1994, Humborg et al. 2000).

Although BMSD has not yet been described in Western Canada or hypereutrophic lakes, several lake specific characteristics indicate that it could occur in Lac la Biche. First, potentially limiting Si concentrations occur transiently in Lac la Biche (Schindler et al., unpublished data). Second, Lac la Biche has a long residence time, with a mean of 28 years (from 1982 through 1995) (Schindler et al., unpublished data). While the lake is polymictic, which should promote Si re-supply from the sediments, Schelske (1985) found only a small percentage of Si (< 5%) must be permanently lost to the sediments in long-residence time systems to effect major shifts in the biogeochemical cycling of Si. Therefore, as a result of eutrophication, Si mediated shifts to include decreasing proportions of diatoms and increasing

proportions of non-siliceous taxa such as Cyanobacteria may have occurred in Lac la Biche.

Similar to what has been reported in some other lakes in subarctic Canada (Stoermer et al. 1990), Europe (Wessels et al. 1999), and in the coastal United States (Turner and Rabalais 1994), BSi concentration and flux have increased with time, but there is no evidence of recent declines in sediment BSi that would indicate Si limitation in Lac la Biche. Severe annual Si depletion to below limiting concentrations may occur on a time scale of less than 5 to greater than 50 years, depending on the degree of nitrogen and phosphorus enrichment, the external input of Si to the system, as well as lake specific characteristics such as depth and water residence time (Schelske et al. 1983, Schelske et al. 1987, Schelske 1999). The increase in nitrogen and phosphorus loading to Lac la Biche may still be insufficient to support a diatom bloom capable of consistently depleting Si reserves. Therefore, Si renewal to the water column through frequent mixing events and tributary inputs is currently sufficient to maintain diatom populations.

Because both Cyanobacteria carotenoid concentrations and BSi concentration and flux rates have increased in more recent sediments, I infer that production of both Cyanobacteria and siliceous algae have increased in the last 50 years. However, there is no indication that a relative shift in phytoplankton community structure to include increasing proportions of Cyanobacteria and decreasing proportions of diatoms occurred with eutrophication. This may be because Si concentrations were not depleted to limiting concentrations or because P loading was insufficient to cause a relative shift in the phytoplankton assemblage.

Schelske et al. (1987) and Verschuren et al. (2002) in Lake Zürich and Lake Victoria respectively, found severe Si depletion and Si limited diatom growth (indicated by stratigraphic peaks in BSi in the sediment record) preceded increases in Cyanobacteria biomass. Further, there is well documented evidence of long-term Si depletion in Lake Michigan (Schelske et al. 1983, Schelske 1999). However, Schelske et al. (1987) state that prolonged Si limited diatom growth was not accompanied by an increase in Cyanobacteria biomass because of low TP concentrations. TP concentrations in Lac la Biche may not have increased sufficiently from background

concentrations to result in relative shifts in the phytoplankton community.

The lack of long term Si depletion or changes in phytoplankton community structure does not preclude changes in the seasonal or transient depletion of Si and phytoplankton succession as a result of eutrophication. Transient Si limitation as was observed in the summer of 2003 in Lac la Biche may not be evident in the sediment record (Schelske et al. 1987) but may alter patterns of seasonal phytoplankton succession from diatom to Cyanobacteria dominated assemblages (Horn and Uhlmann 1995, Chapter 3). Similarly, variation in the timing of seasonal phytoplankton succession that may arise due to transient Si limitation is also unlikely to be resolved from sediment records. However, the recent increase in Si deposition to the sediment increases the probability of Si shortage in the future, and it is possible that seasonal Si depletion as was observed in Lac la Biche in 2003 could signal the onset of more frequent periods of Si limitation (Schelske et al. 1983, Schelske 1999).

Conclusions

Paleolimnological analyses indicate that Lac la Biche was historically productive. Nevertheless, based on evidence of increased total algal biomass and increasing blooms of Cyanobacteria, water quality has declined since 1950. I believe sewage input is a proximate cause of declining water quality based on my observations of increasing TP concentrations, declining TN:TP ratios, the timing of changes in phytoplankton production, and the increase in $\delta^{15}N$ in D1 sediment, which received sewage effluent, compared to D3, which does not. Implementation of tertiary sewage treatment may help to resolve water quality issues in D1. Diffuse sources of nutrient loading such as agricultural run-off are also important (Neufeld 2005), but are more difficult to control because they are dispersed over a large area and vary with weather events (Carpenter et al. 1998).

While there is no historical evidence of prolonged Si depletion events in Lac la Biche, Si depletion may become a more common feature in the lake in the future. Ongoing eutrophication, landscape modifications and changing climatic regimes are expected to affect the frequency and extent of Si depletion in aquatic systems (Turner and Rabalais 1994, Humborg et al. 2000). Without substantial management

intervention, anthropogenic nutrient loading from land clearing, agricultural run-off and sewage effluent as well as internal nutrient loading will continue to contribute to eutrophication and BMSD. Additionally, the majority of Si loading to aquatic systems is via weathering and transport in surface water flow (Tréguer et al. 1995, Schindler et al. 1996). Therefore tributary inputs may be critical in the maintenance of diatom populations, particularly when nutrient enrichment has already resulted in increased Si uptake (Conley and Malone 1992, Humborg et al. 2000).

Areas in Western Canada anticipate lower surface water flow due to drought, climate warming and human induced landscape modifications in this century (Schindler and Donahue 2006). Si loading to lakes declines as stream flow decreases (Schindler et al. 1996). Reduced Si loading, coupled with the effects of eutrophication and BMSD, may increase the frequency of Si depletion events, leading to the restructuring of aquatic environments, even in those systems where short water residence times and mixing regimes would seem to preclude the occurrence of BMSD.

Even in the absence of long-term Si depletion, anthropogenic nutrient enrichment may decrease Si:P and Si:N ratios, which can modify phytoplankton community structure and ecosystem dynamics (Officer and Ryther 1980, Conley and Malone 1992, Egge and Aksnes 1992, Turner et al. 1998). It would be prudent to initiate long-term investigations to determine the nutrient mass balance and patterns in phytoplankton succession in Lac la Biche and other eutrophied lakes to understand how declining surface water flow and eutrophication may interact to affect Si dynamics and the frequency of nuisance algal blooms.

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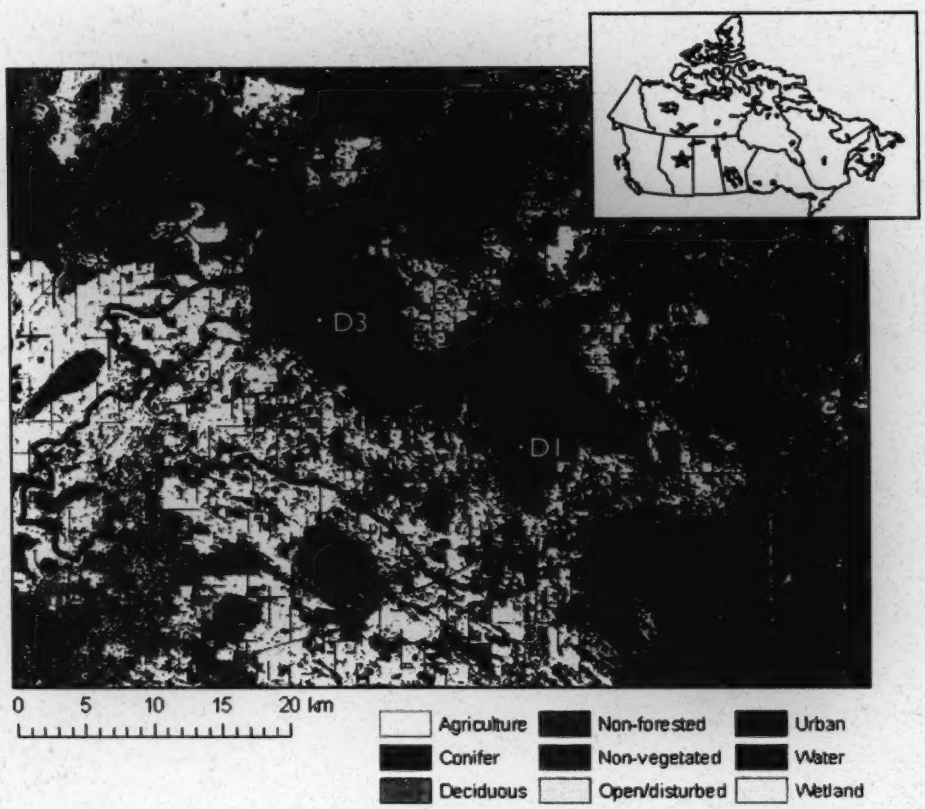

Figure 2.1. Map of the study sites at Lac la Biche. Cores were sampled from the east and west basins at locations D1 and D3 respectively. The location of sewage inflow is marked by the arrow and the immediate catchment is outlined in black.

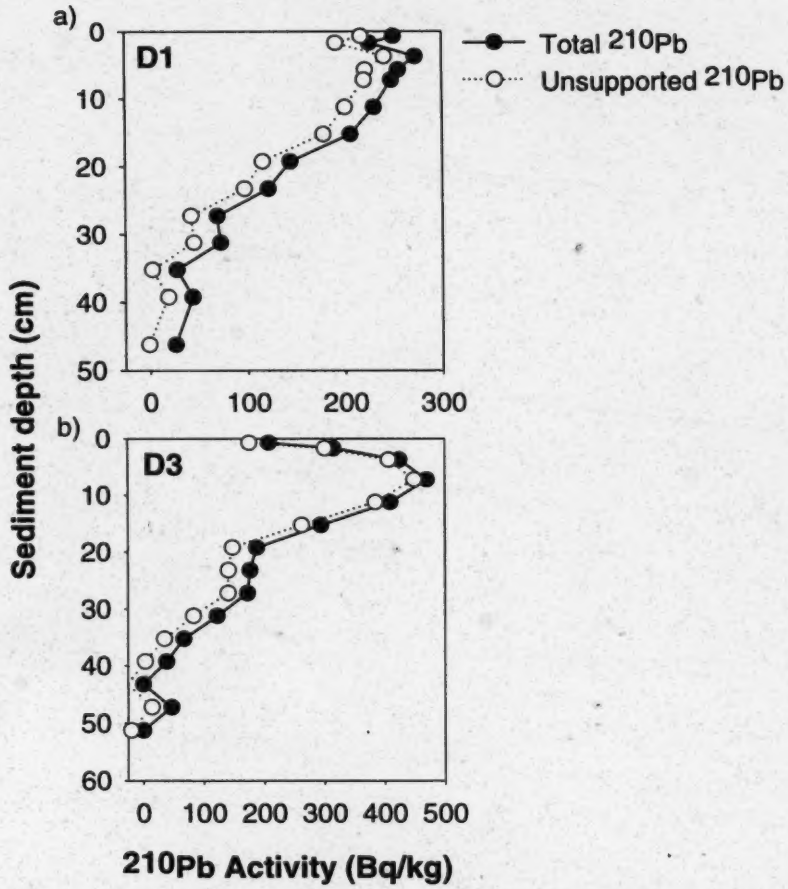

Figure 2.2. The total and unsupported ^{210}Pb activity at various depths in sediment cores collected from a) D1 and b) D3 in Lac la Biche.

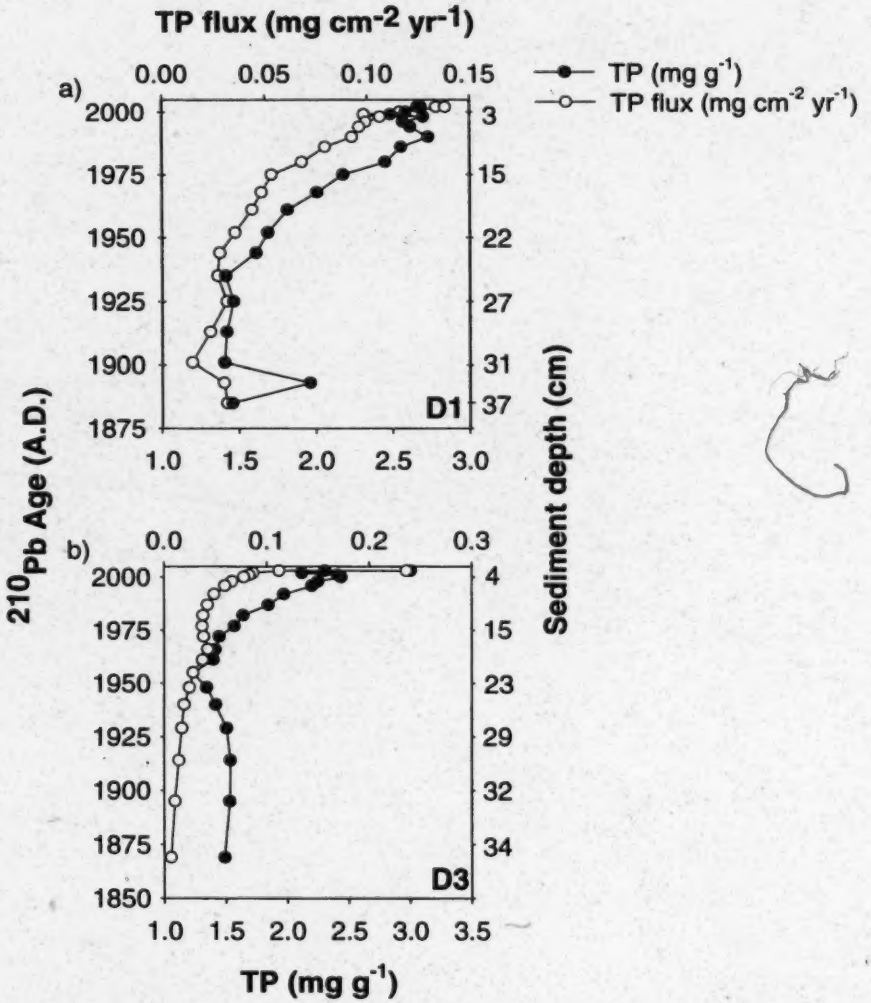

Figure 2.3. TP concentration and flux in sediment cores collected from a) D1 and b) D3 in Lac la Biche.

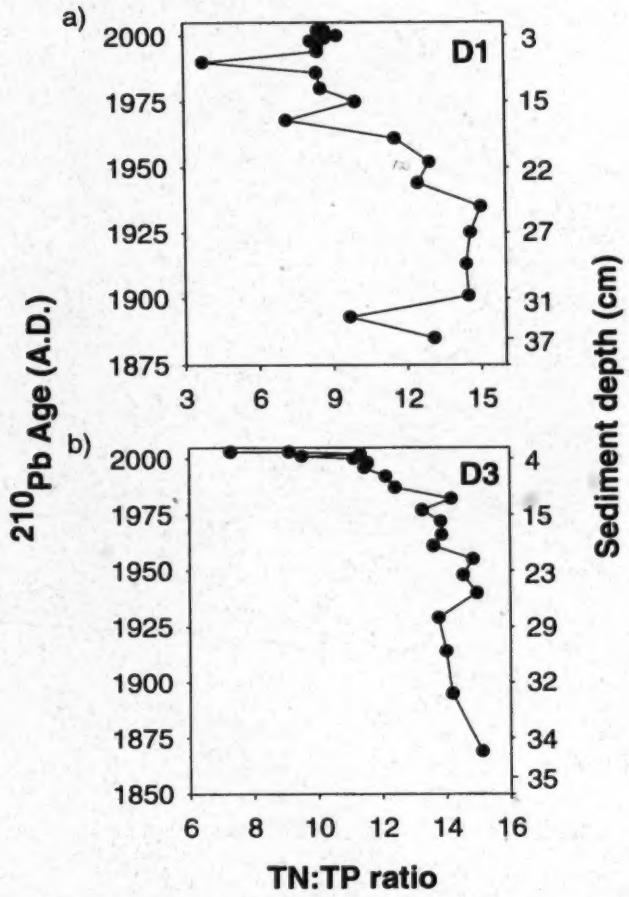

Figure 2.4. TN:TP ratios (by weight) obtained from sediment cores collected from a) D1 and b) D3 in Lac la Biche.

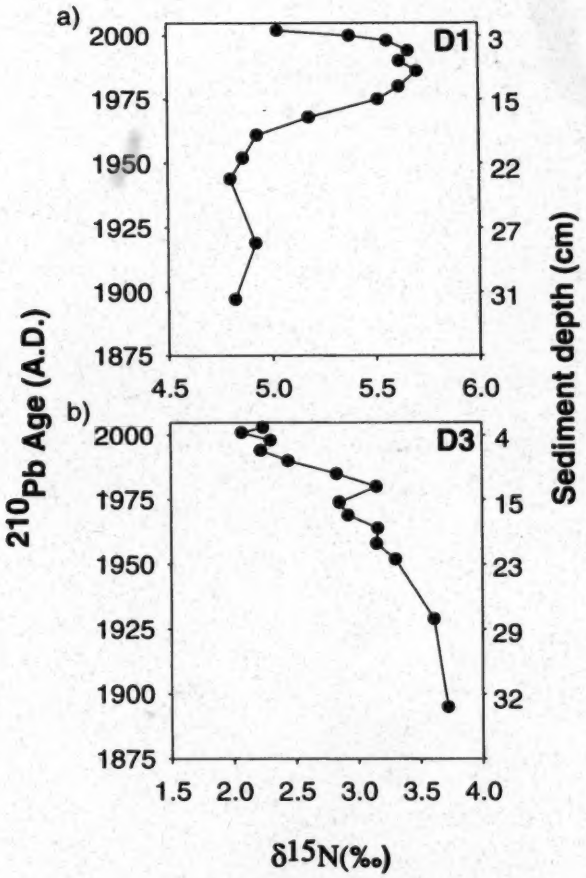

Figure 2.5. δ15N in sediment cores collected from a) D1 and b) D3 in Lac la Biche.

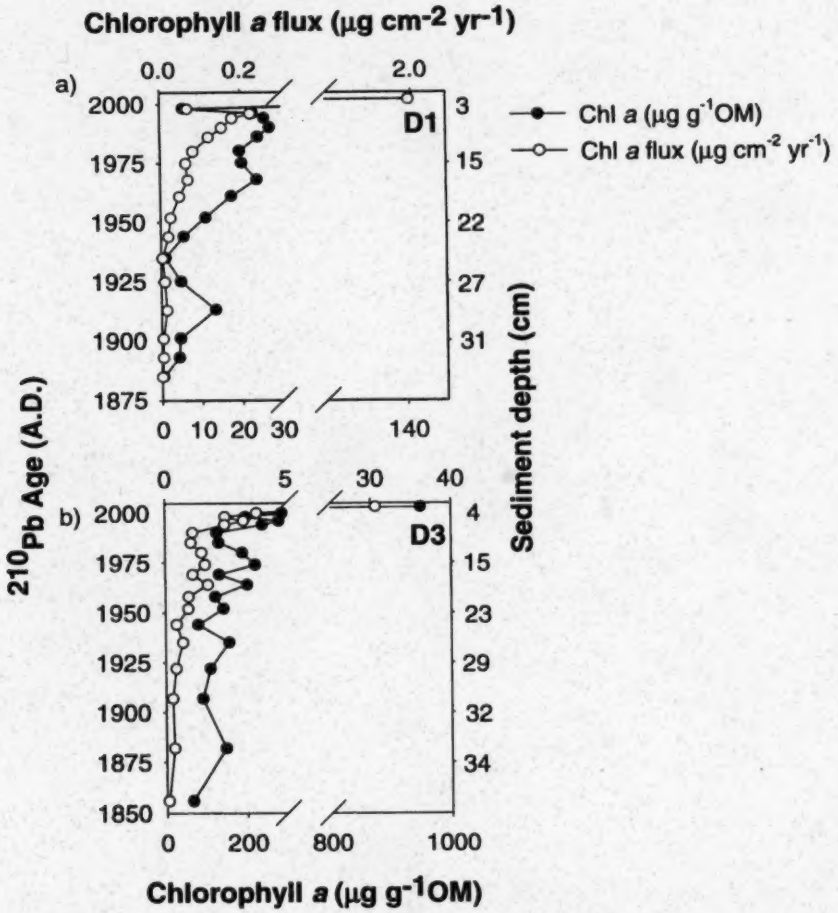

Figure 2.6. Chlorophyll *a* concentrations in sediment cores collected from a) D1 and b) D3 in Lac la Biche.

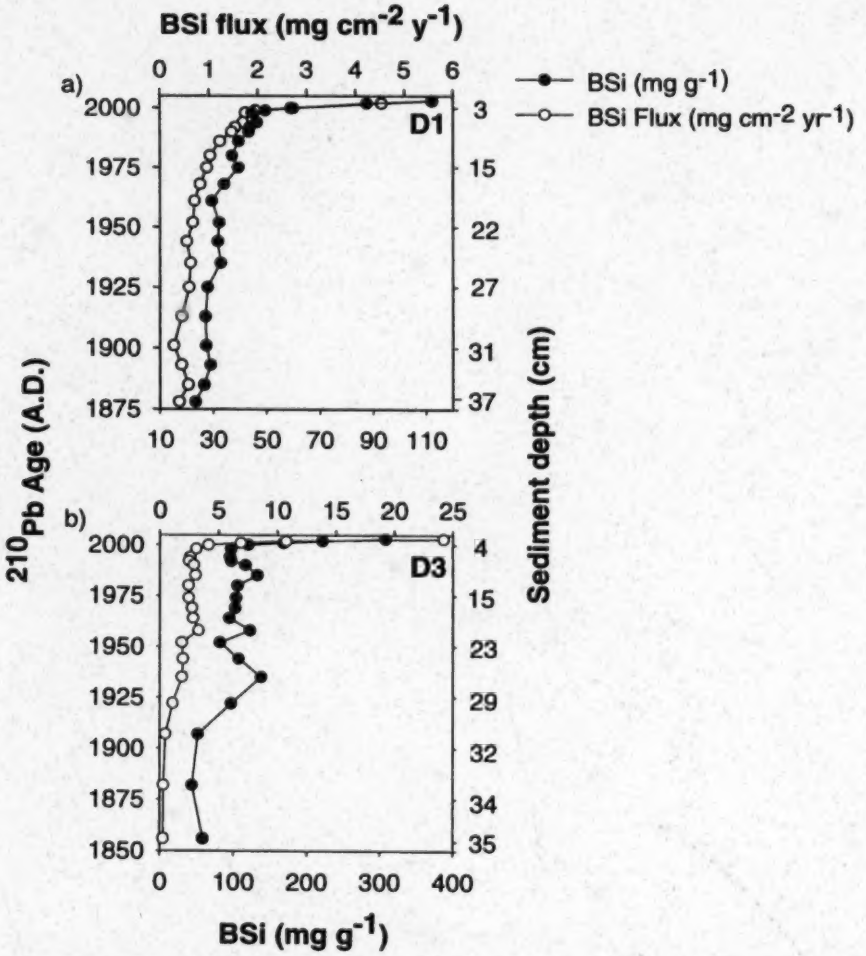

Figure 2.7. BSi concentration and flux in sediment cores collected from a) D1 and b) D3 in Lac la Biche.

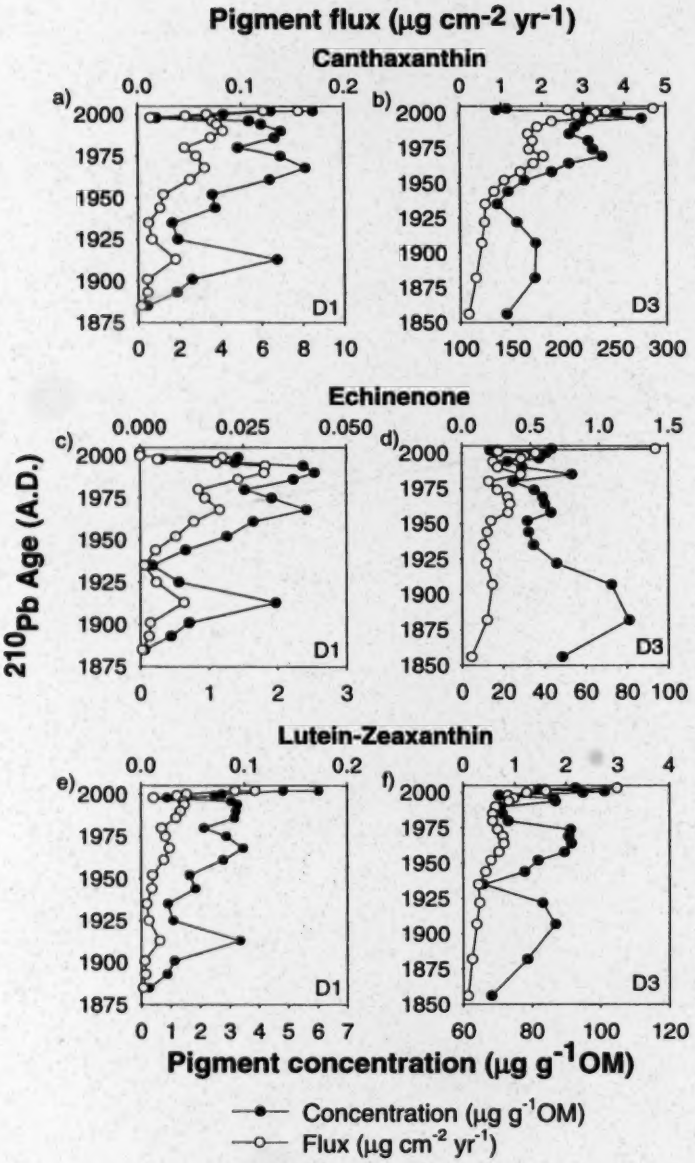

Figure 2.8. Pigment concentrations in sediment cores collected from D1 (a, c, e) and D3 (b, d, f) in Lac la Biche. Pigments analyzed were: a, b) Canthaxanthin; c, d) Echinenone; and e, f) Lutein-Zeaxanthin.

Chapter 3: The effect of Si and N:P amendment on algal community structure and biomass

Introduction

Phosphorus (P) and nitrogen (N) and are critical nutrients regulating phytoplankton production (Schindler 1977, Hecky and Kilham 1998, Schindler 2006). Recent declines in the water quality of lakes in boreal Alberta may be partly attributed to increased loading of these nutrients (Mitchell and Trew 1992). However, dissolved silica (Si) also regulates phytoplankton community structure and production due to its essential role in the production of siliceous algae such as diatoms (Kilham 1971, Officer and Ryther 1980, Conley et al. 1993, Schelske 1999, Rocha et al. 2002). Diatoms are widespread, abundant and are a high quality food source for grazers. Consequently they play an important role in the structuring of aquatic food webs (Round et al. 1990). Because they are enclosed in a silicified wall or frustule, their production is dependent on an adequate supply of Si.

Long term Si depletion can be caused by eutrophication and enhanced diatom production in a process known as biologically mediated silica depletion (BMSD) (Schelske and Stoermer 1971, Schelske et al. 1986, Schelske et al. 2006). With BMSD, increased nutrient loading stimulates diatom production and consequent sedimentation, with a portion of the siliceous frustules becoming permanently sequestered in the sediment. This loss of silica to lake sediment, coupled with more efficient cycling of sediment P relative to Si, results in reduced Si concentrations in the water column, eventually leading to either seasonal or year round Si limitation. The extent and duration of Si depletion can be dependent upon the degree of phosphorus enrichment (Schelske 1999). Modification of the biogeochemical Si cycle may lead to changes in phytoplankton community composition, increasing the proportion of non-siliceous algae such as potentially nuisance Cyanobacteria in freshwater and flagellates in the marine system and decreasing the relative importance of diatoms (Schelske and Stoermer 1971, Officer and Ryther 1980, Egge and Aksnes 1992). Changes in the phytoplankton community structure may additionally alter food web dynamics (Turner et al. 1998, Humborg et al. 2000) and nutrient cycling processes (Smetacek 1985, Conley et al. 1993).

Lac la Biche is a large, shallow, hypereutrophic (total phosphorus (TP) = 40-330 $\mu g\ L^{-1}$, chlorophyll *a* (chl *a*)= 10-180 $\mu g\ L^{-1}$) boreal lake in northern Alberta, Canada, which is undergoing anthropogenic eutrophication (Chapter 2). Residents of the town of Lac la Biche have expressed concern regarding perceived declines in water quality since the 1990's. Their complaints include symptoms most commonly associated with eutrophication such as taste and odour problems, frequent algal blooms and periodic fish kills (Carpenter et al. 1998). There are number of potential factors contributing to water quality decline in the lake. These include a trophic cascade caused by over-exploitation of piscivorous fish, land clearing, agricultural run-off, cottage and urban sewage effluent and silica depletion (Schindler et al., unpublished data, Neufeld 2005). The purpose of this study was to examine the role of silica depletion in the eutrophication of Lac la Biche.

Water chemistry data collected in 2003 indicate that Si concentrations occasionally approach or fall below potentially limiting concentrations (< 0.5 mg L^{-1}, Schelske 1999) in Lac la Biche in the late spring (0.64 mg L^{-1}) and mid- to late summer (0.17 mg L^{-1}), particularly in the basin most affected by anthropogenic eutrophication (Schindler et al., unpublished data). There appears to be significant interannual variation, however, because data from 2004 and 2005 showed no evidence of potentially limiting Si concentrations (Schindler et al., unpublished data).

Ecosystem-specific factors that affect nutrient cycling will determine if a nutrient-enriched system will demonstrate long-term changes in the biogeochemical silica cycle. In freshwater, BMSD has been best documented in large, naturally oligotrophic lakes with long water residence times such as the Laurentian Great Lakes (Conley et al. 1993, Schelske 1999, Conley and Schelske 2001). These lakes are sensitive to low inputs of anthropogenic nutrients and are dimictic, limiting the redistribution of Si from the sediment to spring and fall overturn. Further, due to their long water residence times, steady state external Si input into these ecosystems is insufficient to compensate for its loss as it is deposited and preserved in lake sediments (Conley et al. 1993, Conley and Schelske 2001).

Several lines of evidence suggest that BMSD may occur in a variety of geographically and ecologically disparate systems. Contemporary data sets have

linked eutrophication events with seasonal or long-term declines in Si concentrations in oligotrophic lakes in the UK (Lund 1972, Talling and Heaney 1998), arctic Canada (Welch et al. 1989), and the Laurentian Great Lakes (Schelske 1999), as well as in coastal and marine systems in North America and Europe (Conley et al. 1993, Turner and Rabalais 1994, Humborg et al. 2000, Rocha et al. 2002). Analysis of biogenic silica (BSi) in sediment cores has also been used to infer the onset Si limitation with eutrophication in lakes in Africa (Verschuren et al. 1998), Europe (Schelske et al. 1987) and North America (Schelske 1999).

Finally, numerous marine mesocosm experiments have shown that increased Si:N and/or Si:P ratios result in a higher proportion of diatoms relative to flagellated phytoplankton (Doering et al. 1989, Egge and Aksnes 1992, Sommer 1994, Wassmann et al. 1996, Escaravage et al. 1999, Svensen 2002). Marine experiments have also shown diatom blooms were extended (Doering et al. 1989) or induced (Egge and Aksnes 1992) under a variety of environmental conditions when N and P enriched mesocosms were supplemented with Si above limiting concentrations.

Still, uncertainties remain regarding the effect of environmental and nutrient conditions on BMSD and the phytoplankton community structure. It has been postulated that Si limited diatom growth in P and N enriched systems favours an increase in Cyanobacteria biomass (Schelske and Stoermer 1971). Laboratory and *in situ* experiments conducted in the Laurentian Great Lakes examined changes in Si uptake rates in response to changing P and N input. Phytoplankton community response to changes in Si concentrations were reported as changes in chl *a* concentration, rates of carbon fixation and changes in diatom cell numbers or biomass, but did not include changes to the overall phytoplankton assemblage (Schelske et al. 1974, Schelske et al. 1975, Schelske et al. 1986). Si limited diatom growth in nutrient enriched lakes coincided with increased Cyanobacteria abundance (Schelske et al. 1987, Verschuren et al. 2002). But to date, freshwater experiments have not examined the mechanism responsible for altered algal assemblages following Si depletion as has been done in marine systems. BMSD also has not been studied in eutrophic or hypereutrophic lakes, and it remains unclear whether these systems, which may be less sensitive to increased N and P input, will exhibit BMSD as has been shown previously

in oligotrophic systems.

Neither freshwater nor marine studies have examined the effect of differing N:P ratios, nor have freshwater studies addressed the effect of seasonality on BMSD in *in situ* experiments. Anthropogenic eutrophication resulting in low ambient N:P ratios favours Cyanobacterial growth (Schindler 1977, Smith et al. 1983, Paerl 1996, Dokulil and Teubner 2000). Mid- to late summer temperature, light and mixing regimes are also expected to favour Cyanobacteria (Paerl 1996, Dokulil and Teubner 2000). Therefore, both varying N:P ratios and changing environmental conditions may affect the ability of diatoms to deplete Si concentrations, and may also affect phytoplankton succession following Si depletion.

Welch et al. (1989) conducted a whole ecosystem fertilization experiment in arctic Canada. They found that Si concentrations did not decline in a lake fertilized only with P, while Si did decline in a lake fertilized with both N and P. Schelske et al. (1986) found that changing N:P ratios had little effect on Si uptake and that Si uptake occurred even at low light intensities over a range of temperatures in Laurentian Great Lake waters. However, the authors do not report changes to the phytoplankton assemblage due to Si depletion with changing N concentrations, light intensities and temperature. Therefore, data demonstrating the effect of nitrogen loading and seasonality on the efficacy of BMSD and resulting changes to phytoplankton community structure in freshwater are equivocal or incomplete.

In this chapter I examine these issues in a series of nutrient amendment experiments conducted in mesocosms deployed in Lac la Biche. The objectives were: 1) to determine if potentially limiting Si concentrations could be induced in a hypereutrophic lake; 2) to determine the effect of varying N:P ratios on silica depletion; 3) to determine the consequence of reduced Si concentrations on chlorophyll *a* concentration, phytoplankton biomass and phytoplankton community structure; and 4) to determine if there is a seasonal pattern that affects Si depletion and the resulting phytoplankton assemblage.

Methods

Study Area

Lac la Biche is a large, shallow lake (mean depth = 8.4m, maximum depth = 21.3m) with an area of 234 km^2 and a catchment area of 4040 km^2 (Mitchell and Prepas 1990). It is located at 54° 52' N latitude, 112° 05' W longitude in the mid-boreal mixedwood ecoregion (Strong 1992) in north-central Alberta. Experimental mesocosms were deployed in a small, sheltered bay near Currant Island in the east basin (Figure 3.1).

Experimental Design

To test the effect of the N:P ratio of supplemented nutrients on Si utilization and the effect of N:P ratios and Si concentration on phytoplankton community structure, a 2x3 factorial experiment was performed with two levels of Si addition, none (ambient) and high, and three levels of N and P additions, none (ambient N:P), low N:P and high N:P. Ambient Si concentrations ranged from 0.39 – 15.6 mg L^{-1}, and ambient total dissolved N (TDN) to total dissolved P (TDP) ratios ranged from 5.6 – 78 (by weight) throughout the three experiments. TDN, as opposed to dissolved inorganic N (DIN), was used for N:P ratio calculations because DIN was occasionally below detection limit. Si as $Na_2SiO_3 \cdot 5H_2O$ was added at 6.4 mg L^{-1} in the high Si treatment, or remained at ambient concentrations. N and P were added in concentrations of 905 μg L^{-1} and 100 μg L^{-1} respectively in the high N:P treatment, 181 μg L^{-1} and 100 μg L^{-1} in the low N:P treatment, or remained at ambient concentrations. The N:P ratios by weight in the high (9:1) and low (1.8:1) N:P treatments were selected to span the Redfield N:P ratio of 7:1 (Redfield 1958), and potentially induce phosphorus limitation in the high N:P treatment, and nitrogen limitation in the low N:P treatment. N was added as NH_4NO_3 and P was added as H_3PO_4. Three sequential 21-27 day experiments were conducted, initiating in June (21 days), July (27 days) and August (27 days) 2004.

Mesocosms consisted of 1m x 1m x 3m deep rectangular closed-bottom woven polyethylene bags. A total of 24 mesocosms were deployed in water 3 to 5 m deep, filled with raw lake water and floated from wooden frames approximately 35 cm

above lake level. They were arranged in a straight line from east to west to minimize shading. Treatments were randomly assigned to individual mesocosms to control for confounding effects due to edge and spatial gradients. Experimental groups were comprised of 4 replicates with the exception of the July experiment, where the ambient Si, low N:P treatment was completed with 3 replicates.

Water chemistry, zooplankton and phytoplankton were sampled weekly with a 2.54 cm diameter, 2.75 m long clear plastic tube inserted full length into each mesocosm after stirring. Three tube samples were combined and subsampled. Periphyton samples were collected on 2.5 cm x 2.75 m woven polyethylene strips suspended in each mesocosm. Periphyton was sampled at the mid-point and end of the July and August experiments and preserved in Lugol's solution until analyzed. Water temperature was measured with a thermister. Water chemistry, zooplankton and phytoplankton data were also collected weekly from the lake near the mesocosms.

Water Chemistry and Plankton Analysis

Water samples were collected in acid-washed Nalgene polyethylene containers. Whole water samples were passed through a 125µm – 250 µm sieve to remove large zooplankton prior to bottling and were analyzed for total P (TP), total N (TN), and Si concentrations. The size of the sieve varied due to their availability but did not significantly affect water chemistry results (Crowe, unpublished data). Samples filtered through a 0.45 µm Whatman GF/F filter were analyzed for total dissolved P (TDP), soluble reactive P (SRP), total dissolved N (TDN), ammonium (NH_4^+) and nitrate plus nitrite ($NO_3^- + NO_2^-$) (as per standard methods at the University of Alberta Limnological Services Unit, Edmonton, Alberta, Canada). TN, TDN, NH_4^+ and $NO_3^- + NO_2^-$ were analyzed using a Technicon AutoAnalyzer II. TP, TDP and SRP were analyzed colourimetrically with a spectrophotometer. Si as molybdate-reactive silicon was analyzed using a Technicon AutoAnalyzer II. Chl *a* was collected by filtering samples on 0.45 µm Whatman GF/F filters. Filters were protected from light and moisture and stored below 6°C until frozen within 8 hours of sampling. Chl *a* was extracted in ethanol and its concentration determined fluorometrically according to methods of Welschmeyer (1994).

Zooplankton were collected from a 500 mL whole water sample using a 64 μm sieve and preserved in sugared formalin. Phytoplankton were sampled by collecting 250mL of whole water and were preserved in Lugol's solution. To identify and enumerate phytoplankton, sub-samples were gravity settled for 24 hours. Counts were performed using the Ütermohl technique as modified by Nauwerck (1963) on an inverted microscope at magnifications of 125X, 400X and 1200X with phase contrast illumination. Cell counts were converted to wet biomass using cell volume and assuming a specific gravity of 1. Estimates of cell volume for each species were obtained by measurements of up to 50 cells of an individual species and applying the geometric formula best fitted to the shape of the cell (Vollenweider 1968; Rott 1981).

Zooplankton were enumerated using a dissecting microscope at 16X and 40X magnification. All crustacean zooplankton present in each sample were identified and enumerated. Copepods were identified to subclass and cladocerans to genus. Rotifers were identified to genus and were enumerated by either counting the entire sample, or enumerating successive 10 mL aliquots until a total of 100 individuals were enumerated. Zooplankton lengths were measured using a calibrated ocular micrometer. The dry weight of each taxon was estimated using length-weight regressions (Bottrell 1976) or, in the case of rotifers, genus-specific approximations of individual biomass (Malley et al. 1989).

Periphyton dry mass and ash-free dry mass (AFDM) were determined for the July and August experiments. Periphyton collected on 2.5 cm x 75 cm woven polythethylene strips suspended in each mesocosm was scraped using a razor scraper and concentrated on a 0.45μm Whatman GF/F filter. Samples were dried at 105°C for 24 hours in tared aluminum trays to estimate total dry mass. The samples were subsequently combusted for 1 hour at 500°C, then wet and re-dried for 24 hours at 105°C to reintroduce the water of hydration in clay and AFDM (Steinman and Lamberti 1996).

Statistical Analysis

Statistical analyses were performed with SPSS 13.0 software. Two factor analysis of variance was used to determine differences among treatment groups on the

final day of each experiment. Repeated measures analysis of variance (RM-ANOVA) was performed to test for the time dependent effects of nutrient treatments. A multifactor analysis of variance (MANOVA) was used to test for differences in the phytoplankton community response to experimental treatments. Models used in MANOVA analyses were determined by including taxa that comprised greater than 90% of the total phytoplankton biomass. Statistical significance was determined at $\alpha = 0.05$. Tukey's test was used for post hoc analysis to determine significant differences between treatment groups. Si, chl *a* concentrations and biomass data were log10 (x+1) transformed prior to statistical analysis to improve normality and homogeneity of variances.

Results

Nutrient Treatments

Both high N:P and low N:P treatments significantly lowered the TDN:TDP ratios compared to ambient N:P treatments for all three experiments (RM-ANOVA: $F_{2,18} = 10.42$, p=0.001, (June) ; $F_{2,17}=18.65$, p<0.001 (July); and $F_{2,18}=58.01$, p<0.001 (August); Figure 3.2). The high Si treatment significantly elevated Si concentrations above the ambient Si treatment in all three experiments (RM-ANOVA: $F_{1,18} = 78.69$, p<0.001 (June); $F_{1,17}=575.85$, p<0.001 (July); and $F_{1,18}=1095.68$, p<0.001 (August); Figure 3.3). There were no significant interactions between Si and N:P treatment on the resulting TDN:TDP ratios (RM-ANOVA: $F_{2,18} = 3.31$, p=0.059 (June); $F_{2,17}=0.27$, p=0.769 (July); and $F_{2,18}=2.56$, p=0.105 (August)) or Si concentrations (RM-ANOVA: $F_{2,18} = 0.40$, p=0.673 (June); $F_{2,17}=0.50$, p=0.614 (July); and $F_{2,18}=1.52$, p=0.25 (August)) in any experiment.

The mean ambient water temperatures throughout the June, July and August experiments were 16.5°C, 20.4°C and 17.7°C respectively.

Nutrient-induced Si depletion

There was a significant effect of N:P treatment on Si concentrations on day 14 in June and day 20 in July when Si concentrations decreased to the lowest values in ambient Si treatments (ANOVA: $F_{2,18}=28.75$, p<0.001 (June); $F_{2,17}=7.47$, p=0.005

(July); Figure 3.4 a,b). There was no significant effect of N:P amendment on Si concentrations in the August experiment (ANOVA: $F_{2,18}$=1.104, p=0.353; Figure 3.4c).

In June, Si concentrations declined to a significantly greater extent in ambient Si mesocosms subjected to the high N:P treatment compared to either ambient (Tukey's: p<0.001) or low N:P (Tukey's: p<0.001) treatment. There was no significant difference in Si concentrations between ambient N:P and low N:P treatments (Tukey's: p=0.062). In the July experiment, however, Si concentrations declined to a significantly greater degree in the ambient N:P treatment compared to the high N:P treatment (Tukey's: p=0.007). There were no significant differences in Si concentrations between the ambient N:P and low N:P treatments (Tukey's: p=0.297) or low N:P and high N:P treatments (Tukey's: p=0.176).

Si concentrations declined to 0.06 mg L^{-1}, well below potentially limiting concentrations of <0.5 mg L^{-1} (Schelske 1999), in the June mesocosms subjected to ambient Si, high N:P treatments (Figure 3.4a). Initial Si concentrations rose with each subsequent experiment. Therefore, although Si concentrations declined in ambient Si treatments throughout all three experiments, Si concentrations did not decline to potentially limiting concentrations in either the July or August experiment. The mean Si concentration did not fall below 0.94 mg L^{-1} and 6.7 mg L^{-1} in any treatment in the July and August experiments respectively (Figure 3.4 b,c).

Chlorophyll a and Phytoplankton Biomass

Chl *a* concentrations were significantly lower in high Si compared to ambient Si treatments in the July and August experiments (RM-ANOVA: $F_{1,18}$=2.83, p=0.110 (June); $F_{1,17}$=14.2, p=0.002 (July); $F_{1,18}$=41.03, p <0.001 (August); Figure 3.5). Chl *a* concentrations are routinely used as a proxy for phytoplankton biomass, but chl *a* and phytoplankton biomass may not always be well correlated (Canfield et al. 1985, Parker and Schindler 2006). As phytoplankton biomass was determined only for the final day of each experiment, I calculated the correlation coefficient between chl *a* and phytoplankton biomass. There was a significant positive relationship between chl *a* and phytoplankton biomass for the final day of the experiments (r=0.8, p<0.001;

Figure 3.6). Therefore, similar to chl *a* concentrations, I infer that phytoplankton biomass was lower in high Si than ambient Si mesocosms throughout both the July and August experiments, as was shown with chl *a*. This inference is further supported by a trend illustrating lower phytoplankton biomass in high Si mesocosms on the final day of the experiment, though it was statistically significant only for the August experiment (ANOVA: $F_{1,18}$=4.19, p=0.055 (June); $F_{1,18}$=0.87, p=0.364 (July); $F_{1,18}$=22.34, p<0.001 (August); Figure 3.7).

There were significant effects of N:P treatment on chl *a* concentrations in the June experiment only. In June, the ambient N:P treatments had significantly lower chl *a* concentrations than either the low or high N:P treatments (RM-ANOVA: $F_{2,18}$=16.69, p<0.001 (June); $F_{2,17}$=2.36, p=0.125 (July); $F_{2,18}$=1.16, p=0.337 (August)). N:P treatment did not significantly affect total phytoplankton biomass in any experiment (ANOVA: $F_{2,18}$=1.96, p=0.170 (June); $F_{2,17}$=0.55, p=0.585 (July); $F_{2,18}$=0.511, p=0.608 (August)). There were also no significant interactions between Si and N:P treatments for either chl *a* concentration (RM-ANOVA: $F_{2,18}$ = 1.32, p=0.293 (June) ; $F_{2,17}$=0.703, p=0.509 (July); and $F_{2,18}$=1.21, p=0.320 (August)) or phytoplankton biomass (ANOVA: $F_{2,18}$=0.089, p=0.915 (June); $F_{2,17}$=0.135, p=0.716 (July); $F_{2,18}$=0.702, p=0.509 (August)).

Phytoplankton Community Changes

A) Broad taxonomic responses

The initial phytoplankton community in June was dominated by chrysophytes and diatoms, followed by cryptophytes, Cyanobacteria and dinoflagellates (Figure 3.8). This contrasts with the July and August experiments where mesocosms were innoculated with Cyanobacteria biomass that was two to three orders of magnitude greater than all other taxa (Figures 3.9, 3.10).

To determine the effects of Si and N:P treatment on the biomass of phytoplankton taxa, I examined those taxa that comprised >90% of the phytoplankton biomass on final day of each experiment. In June, the only statistically significant trend was higher cryptophyte biomass in high N:P treatments (MANOVA: $F_{2,18}$=4.256, P=0.031; Figure 3.8). However, on the final day of the July and August

experiments, mesocosms subjected to high Si treatment demonstrated significant reductions in Cyanobacteria biomass (MANOVA: $F_{1,17}$=5.035, P=0.038 (July); $F_{1,18}$=19.35, P<0.001 (August); Figures 3.9, 3.10). In addition, there was lower chlorophyte biomass (MANOVA: $F_{1,17}$=5.41, P=0.033) and higher diatom biomass (MANOVA: $F_{1,17}$=14.65, P=0.001) in high Si treatments in the July experiment (Figure 3.10). There were no significant effects of N:P treatment (MANOVA: $F_{6,32}$=1.32, P=0.276 (July); $F_{6,34}$=1.32, P=0.277 (August)) or significant Si and N:P interactions (MANOVA: $F_{6,32}$=1.22, P=0.324 (July); $F_{6,34}$=0.83, P=0.558 (August)) in either the July or August experiments.

B) Algal genera responses

Changes in the phytoplankton community in response to experimental treatment was examined using genera that represented >90% of the total phytoplankton biomass in each experiment. The predominant Cyanobacteria genera in the June experiment were *Anabaena spp.* and *Aphanizomenon spp.*, which were dominated by the species, *Anabaena flos-aquae, Anabaena lemmermannii* and *Aphanizomenon flos-aquae. Aphanizomenon spp.* was the most common Cyanobacteria genus in July and August, and was dominated by *Aphanizomenon flos-aquae*. The predominant diatom genera in all three experiments were *Nitzschia spp.* and *Fragilaria spp.* which were dominated by *Nitzschia palea* and *Fragilaria crotonensis*.

There were significant effects of Si treatment on the biomass of phytoplankton genera in all three experiments. In the June and July experiments, an increase in the relative proportion of diatoms was caused both by a decline in the biomass of Cyanobacteria, *Anabaena spp.* in June (MANOVA: $F_{1,18}$=11.2, P=0.004); and *Aphanizomenon spp.* in July (MANOVA: $F_{1,17}$=5.05, P=0.038) and an increase in the biomass of diatoms, predominantly *Nitzschia spp.* in June (MANOVA: $F_{1,18}$= 6.01, P=0.025) and *Fragilaria spp.* and *Nitzschia spp.* in July (MANOVA: $F_{1,17}$=5,28, P=0.035 (*Fragilaria spp.*); $F_{1,17}$=10.80, P=0.004 (*Nitzschia spp.*); Figure 3.11 a,b).

The overall change in phytoplankton community structure was greatest in July. At the beginning of the experiment, more than 95% of the phytoplankton biomass in

all treatment groups was comprised of Cyanobacteria (Figure 3.9). At the conclusion of the 4 week experiment, the diatom biomass in the high Si, ambient N:P treatment was 80% of the total phytoplankton biomass, as opposed to 25% in the ambient Si, ambient N:P treatments. The change in the relative proportion of diatoms and Cyanobacteria with supplemented Si in the ambient N:P treatment was caused both by decreased production of *Aphanizomenon spp.* and increased production of *Fragilaria spp.*. This demonstrates that depleted diatom populations can recover with increased Si under the ambient N:P regime (Figure 3.11 b).

In contrast, in the July high Si, high N:P treatments total phytoplankton biomass was reduced compared to the ambient Si, high N:P treatment. This reduction was caused by a decrease in the biomass of *Aphanizomenon spp.* without a substantial increase in the biomass of diatoms (Figure 3.11 b). The biomass of *Aphanizomenon spp.* was reduced from 3300 mg m^{-3} in the ambient Si, high N:P treatment to 207 mg m^{-3} in the high Si, high N:P treatment, whereas the biomass of all diatom genera increased from 47 mg m^{-3} to only 70 mg m^{-3}. This result is similar to the August experiment where there was a significant decline in the biomass of *Aphanizomenon spp.* in high Si treatments (MANOVA: $F_{1,18}$=19.07, P<0.001), despite no significant increase in diatom biomass (Figure 3.11 c).

Zooplankton and Periphyton Responses

Zooplankton were comprised of predominantly cyclopoid and calanoid copepods in June and *Daphnia spp.* in July and August. Differences in grazing pressure seem unlikely to have caused declines in Cyanobacteria biomass as the size (>30 μm) of the predominant phytoplankton genera in the final two experiments, *Aphanizomenon spp.* and *Fragilaria spp.*, rendered them largely ungrazable (Reynolds 1984). In addition, there was no significant difference in total zooplankton biomass between the mesocosms containing ambient and high Si for the June or July experiments (ANOVA: $F_{1,18}$=2.64, p=0.122 (June); $F_{1,17}$=0.73, p=0.404 (July)), and high Si treated mesocosms had significantly lower zooplankton biomass than ambient Si mesocosms in the August experiment (ANOVA: $F_{1,17}$=15.35, p=0.001; Figure 3.12). There was also little difference in zooplankton community structure among

treatment groups (Crowe, unpublished data).

Changes in phytoplankton community structure are also unlikely to be attributable to changes in periphyton growth. There were no significant differences in periphyton AFDM between ambient and high Si treatments for either the July or August experiments (ANOVA: $F_{1,16}$=0.021, p=0.887 (July); $F_{1,18}$=3.67, p=0.072 (August); Figure 3.13). While it is possible that periphyton community structure differed between ambient and high Si bags independent of changes in the overall biomass, preliminary analysis of the periphyton community structure does not support this possibility (Crowe, unpublished data).

Discussion

Nutrient-induced Si utilization

I show that enhanced N and P input can seasonally induce Si utilization and lead to potentially limiting Si concentrations in experimental hypereutrophic mesocosms. In June, the addition of N and P in a 9:1 ratio resulted in significantly higher Si utilization than either the 1.8:1 or ambient N:P treatments. However, addition of N and P did not enhance Si uptake in the mid to late summer experiments.

My results are consistent with research from oligotrophic lakes where nutrient enrichment resulted in increases in Si uptake in laboratory (Schelske et al. 1984, Schelske et al. 1986) and *in situ* experiments (Schelske et al. 1975). However, contrary to my results, experiments in oligotrophic lakes showed that small additions of P, irrespective of the N:P ratio of the supplemented nutrients, caused increased Si uptake (Schelske et al. 1986). I found that the high N:P treatment in June significantly depleted Si concentrations below those of the low N:P treatment, although both treatments received the same concentration of P.

Si utilization may not have been stimulated in N:P enriched mesocosms in the July or August experiments because low TDN:TDP ratios (near or below 7:1) in both the low and high N:P treatments during the last half of the July experiment, and in all treatments in the August experiment, suggest potential nitrogen limitation (Redfield 1958). Low N:P ratios have been shown to favour the growth of nitrogen-fixing Cyanobacteria such as *Aphanizomenon flos-aquae* (Schindler 1977, Smith 1983,

Dokulil and Teubner 2000), which formed >95% of the phytoplankton biomass at the beginning of both of the July and August experiments. Cyanobacteria may have also been favoured by warmer mid-to late summer temperatures (Paerl 1996, Dokulil and Teubner 2000). I suggest that diatoms were unable to increase production sufficiently to deplete Si concentrations under this combination of unfavourable conditions. However, in the absence of N limitation and with supplemented Si, diatoms increased production sufficiently to significantly reduce the Si concentration in the June high N:P and in the July ambient N:P treatment.

Low initial biomass and a low relative proportion of diatoms may have also inhibited Si utilization in the August experiment. The biomass of diatoms innoculated into mesocosms decreased from 138 mg m^{-3} in July to 58 mg m^{-3} in the August experiment. In contrast, the biomass of Cyanobacteria in the innoculum increased from 25156 mg m^{-3} in the July experiment to 39263 mg m^{-3} in August. The density of Cyanobacteria was also 50X greater than diatoms in July, whereas in August Cyanobacteria density was >1300X greater than diatoms. The reduced relative contribution of diatoms to the phytoplankton assemblage in August may have prevented them from depleting Si concentrations in response to N:P enrichment as was seen in the June experiment. However, Egge and Aksnes (1992) found that diatom populations came to dominate the phytoplankton assemblage in marine mesocosms even when the initial concentration of flagellates was greater than 10000X that of diatoms. Therefore, at least in the marine environment, it is possible for diatoms to increase production sufficiently to dominate flagellates even when they form an extremely small proportion of the initial community.

In summary, I have shown that hypereutrophic systems can demonstrate BMSD, at least on a seasonal basis. Further, I suggest that increased Si utilization in some systems may only occur when nitrogen is not limiting. This is supported by the results of Welch et al. (1989), who reported that Si utilization in experimentally eutrophied lakes occurred only in the lake supplemented with N and P as opposed to P alone. Egge (1998) found in marine experiments that diatoms would not increase production sufficiently to dominate the phytoplankton community under low P conditions, although Si and N were provided in excess. Therefore both the absolute

amount of N and P, as well as ratio in which they are loaded may impact the severity of BMSD in marine and freshwater systems (Doering et al.1989, Sommer 1994, Turner et al. 1998, Schelske 1999, Gilpin et al. 2004). Given the apparent ubiquity of BMSD and the possibility of altering existing N:P ratios with continued eutrophication, further studies that examine the effect of N:P ratios on BMSD are warranted.

Phytoplankton Biomass and Community Changes

I found an increase in the biomass of diatom genera in the June and July experiments when mesocosms were supplemented with Si. This is consistent with many other studies which reported diatom productivity increased with Si addition (Schelske et al. 1986, Welch et al. 1989, Doering et al. 1989, Egge and Aksnes 1992, Wassmann et al. 1996, Svensen 2002). Further, the results of the July experiment confirm the findings of Egge and Aksnes (1992) who found that with supplemented Si, severely depleted diatom populations can recover to dominate the phytoplankton community. In the August experiment, there was no significant increase in diatom biomass in response to Si addition. This may be due in part to low N:P ratios and temperature regimes that favoured the growth of Cyanobacteria (Paerl 1996, Dokulil and Teubner 2000). Additionally, there was a late summer decline in total phytoplankton biomass both in the mesocosms and the nearby lake sampling site. Total phytoplankton biomass in the lake declined by more than an order of magnitude throughout the August experiment, from 39402 mg m^{-3} to 3091 mg m^{-3}. This decline in phytoplankton productivity likely also contributed to the lack of a significant increase in diatom biomass in response to Si amendment.

The overall decline in chl *a* concentration, total phytoplankton biomass and the biomass of Cyanobacteria that occurred in response to Si addition has not, to my knowledge, been previously reported. Results have been consistent among laboratory and mesocosm experiments (Schelske et al. 1986, Doering et al.1989, Egge and Aksnes 1992, Wassman et al. 1996, Svensen 2002) as well as freshwater, coastal and marine ecosystems (Welch et al. 1989, Humborg et al. 2000, Rocha et al. 2002) that Si addition increases chl *a* concentration, primary production, cell counts and/or

phytoplankton biomass as a result of higher diatom production (Schelske et al. 1986, Doering et al.1989, Egge and Aksnes 1992, Wassman et al. 1996, Svensen 2002).

I hypothesized that zooplankton grazing pressure or periphyton production that competed with phytoplankton for available nutrients caused the decline in Cyanobacteria biomass independent of major changes in other phytoplankton taxa. However, given the large size of the dominant algal taxa, and the lack of increase in total zooplankton biomass between ambient and high Si mesocosms, it is unlikely grazing pressure reduced Cyanobacteria biomass in the high Si treatments. Similarly, there were no significant differences in periphyton biomass in ambient versus high Si treatments. It is therefore doubtful that either grazing pressure or periphyton production caused the observed decline in Cyanobacteria biomass.

It is also unlikely that bias in the methodology used to estimate phytoplankton biomass accounts for the observed results. A specific gravity of one was assumed for all enumerated taxa to estimate phytoplankton biomass. This may slightly overestimate Cyanobacteria biomass with respect to diatoms because Cyanobacteria have gaseous vacuoles for buoyancy regulation that would be expected to lower their specific gravity. However, results from the August experiment clearly show the decline in overall phytoplankton biomass in high Si treatments was caused by a decline in Cyanobacteria alone. Therefore any bias in estimating relative phytoplankton biomass would have affected both ambient and high Si treatments equally. Although marine experiments have used $Na_2SiO_3 \cdot 5H_20$ to supplement Si in experimental mesocosms and have not reported similar effects on flagellated phytoplankton (Svensen 2002, Gilpin et al. 2004), perhaps elevated concentrations of either Na (data not shown) or Si from $Na_2SiO_3 \cdot 5H_20$ additions inhibited Cyanobacteria growth. While I used analytical grade chemical, I also cannot rule out the possibility that the chemical itself was contaminated, resulting in a toxic effect on Cyanobacteria.

Although Si concentrations did not decrease below potentially limiting concentrations of 0.5 mg L^{-1} (Schelske 1999) in the July ambient Si, ambient N:P treatment, the biomass of diatoms (primarily *Fragilaria crotonensis*) was significantly lower than in the high Si, ambient N:P treatment. This suggests that Lac la Biche diatoms, specifically *Fragilaria crotonensis*, become Si limited at concentrations

which exceed 0.5 mg L^{-1}. The estimate of the concentration of Si that is limiting is based on K_{hm}, the Si concentration at which diatom growth rate is 90% of its maximum. However, Tilman et al. (1982) show that K_{hm} for many species is likely to be higher than 0.5 mg L^{-1} (though not for *Fragilaria crotonensis*). In addition, Lin and Schelske (1978) reported that K_{hm} may increase seasonally with warmer temperatures. The July experiment reported here had the highest mean water temperature of any of the three experiments. Therefore it is possible that Si limitation occurred at concentrations higher than 0.5
mg L^{-1} in the July experiment.

The ratio of Si:P and/or Si:N, as opposed to the absolute concentration of Si, may have also been an important determinant of phytoplankton succession in these experiments. Horn and Uhlmann (1995) showed Si:P ratios are important in the regulation of diatom-Cyanobacteria succession in a reservoir, and it has also been well documented in marine experiments that Si:N ratios can influence the structure of the phytoplankton community (Doering et al. 1989, Sommer 1994, Humborg et al. 2000).

Seasonality

I found that patterns of Si depletion and taxonomic changes in the phytoplankton community changed throughout the season. Si depletion resulting in Si concentrations that approached or fell below potentially limiting concentrations occurred only in June and July. Diatoms as a group increased in response to Si addition in July only, while significant declines in Cyanobacteria biomass occurred in all three experiments. However, I cannot determine conclusively if differences between experiments were the result of changing the length of the experiment, seasonal climatic changes, the initial species composition or the onset of N limitation.

There were no substantative changes in either total phytoplankton biomass or phytoplankton community structure in June compared to the July and August experiments. This was surprising, given that diatoms comprised 47% of the initial total phytoplankton biomass in June and less than 5% in July and August. The initial diatom biomass was also higher in June (305 mg m^{-3}) compared to either the July (138 mg m^{-3}) or August (58 mg m^{-3}) experiments. Therefore, more diatoms were present in

June to potentially deplete Si concentrations. It is unlikely that the small response of the June diatom community was caused by a shorter incubation period compared to the two later experiments (21 vs. 27 days). Maximum differences in chl *a* concentrations were reached by day 12-14 in all experiments, and severe Si depletion occurred in June by day 14. Additionally, Egge and Aksnes (1992) reported substantial changes to the phytoplankton community within one week of Si supplementation. However, because phytoplankton biomass was determined only for the final day of each experiment, I cannot exclude the possibility that the phytoplankton community changes that were observed in July and August occurred between day 21 and day 27. In addition, TDN:TDP ratios in June in both the ambient N:P and high N:P treatments were likely to be P limited (>9:1) and, as in the July ambient N:P treatment, should favour diatom production. Nevertheless, despite favourable TDN:TDP ratios, a high initial biomass of diatoms and sufficient time, diatom production did not increase to the extent seen in the July high Si, ambient N:P treatments. It is therefore probable that lower June water temperatures, and therefore likely diatom growth rates, prevented the significant increase in diatom production in high Si treatments that was seen in July.

Climatic variables (temperature, water column stability), the onset of N limitation later in the season, differences in the initial phytoplankton community or some combination thereof may have caused prevented diatom community recovery in Si supplemented mesocosms in the August experiment. Water temperature was lower in August than July, and it is unlikely that the sheltered location where the mesocosms were located was subject to substantial variation in mixing regimes throughout the summer. Therefore it is improbable that these climatic factors inhibited diatom recovery in the August experiment. In addition, Egge and Aksnes (1992) found that diatom populations could recover sufficiently to replace flagellate dominated communities year round, dependent only on the availability of Si. However, their study did not test for the effect of N or P limitation, and was conducted in the marine environment, where taxon specific influences of light, temperature and mixing would be expected to have have different effects on phytoplankton growth dynamics. As they found diatoms recovered from even lower initial concentrations and in a shorter

timespan, the structure of the initial phytoplankton community likely did not inhibit diatom recovery in the August experiment. Therefore I suggest the difference in phytoplankton community structure between the July and August experiments was predominantly caused by the onset of N limitation.

Conclusion

I have shown that BMSD can occur, at least on a seasonal basis, in mesocosms in a hypereutrophic lake. In addition, the ability of the diatom community to increase production, and therefore the extent to which Si concentrations are reduced, appears to be greater at high TDN:TDP ratios. Si amendment also caused significant changes to the phytoplankton community, increasing the relative proportion of diatoms and decreasing the relative proportion of Cyanobacteria.

I note that there were no significant interactions between the Si and N:P treatments for any of the experiments, suggesting that the same pattern of phytoplankton growth and succession in response to Si amendment occurred regardless of N:P treatment. However, where N was not potentially limiting, BMSD was increased and Si utilization increased to the extent that Si concentrations may have become limiting. Where N was potentially limiting, the effect of BMSD was minimized and Cyanobacteria dominated.

Based on Si concentration data collected from surveys of Lac la Biche between 2003 and 2005, it appears that Si depletion events occur only occasionally (Schindler et al., unpublished data). Under current levels of N, P and Si loading, it seems unlikely that declining Si concentrations will play an important role in the structuring of the phytoplankton community in Lac la Biche in the near future. However, Si depletion to below potentially limiting concentrations as was seen in Lac la Biche in 2003 coincided with the highest P loading of the three years of survey data. Additionally, Schelske (1999) found that the frequency and duration of Si depletion was proportional to the degree of eutrophication in the Laurentian Great Lakes. Therefore, with increased nutrient loading, Si depletion may become a more consistent feature in Lac la Biche. Without substantial management intervention, anthropogenic nutrient loading from land clearing, agricultural run-off, sewage effluent as well as

ongoing internal nutrient loading will continue to contribute to widespread eutrophication and BMSD.

Long term Si decline may also be caused by a reduction in Si loading (Conley and Malone 1992, Humborg et al. 2000). The majority of external Si loading to aquatic systems is via Si weathering and transport in surface water flow (Tréguer et al. 1995). Si supplied to lakes decreases as stream flow decreases with drought and climate warming (Schindler et al. 1996). Areas in Western Canada are anticipated to have lower surface water flow in the future due to drought, climate warming and human induced landscape modifications in this century (Schindler and Donahue 2006). Therefore, although the future impacts of climate warming on Si cycling are unclear, with decreased surface water flow I may expect a widespread decline in Si loading to aquatic systems (Conley and Malone 1992, Schindler et al. 1996, Humborg et al. 2000). Reductions in silica loading, coupled with the effects of eutrophication and BMSD, may increase the importance of Si depletion in restructuring aquatic environments, even in those systems where short water residence times and frequent mixing regimes would seem to preclude BMSD.

In summary, I have shown that BMSD can occur in hypereutrophic lakes in response to increased N and P loading. Further, Si concentrations may play an important role in the composition of the phytoplankton communities. Finally, declining Si concentrations may favour the blooms of potentially toxic Cyanobacteria, particularly at low N:P ratios. Changes to the phytoplankton community structure as a result of changing Si concentrations may impact the food web, affecting culturally and economically valuable fish stocks (Turner and Rabalais 1998) and may exacerbate taste and odour problems, anoxia and potentially toxic algal blooms associated with eutrophication.

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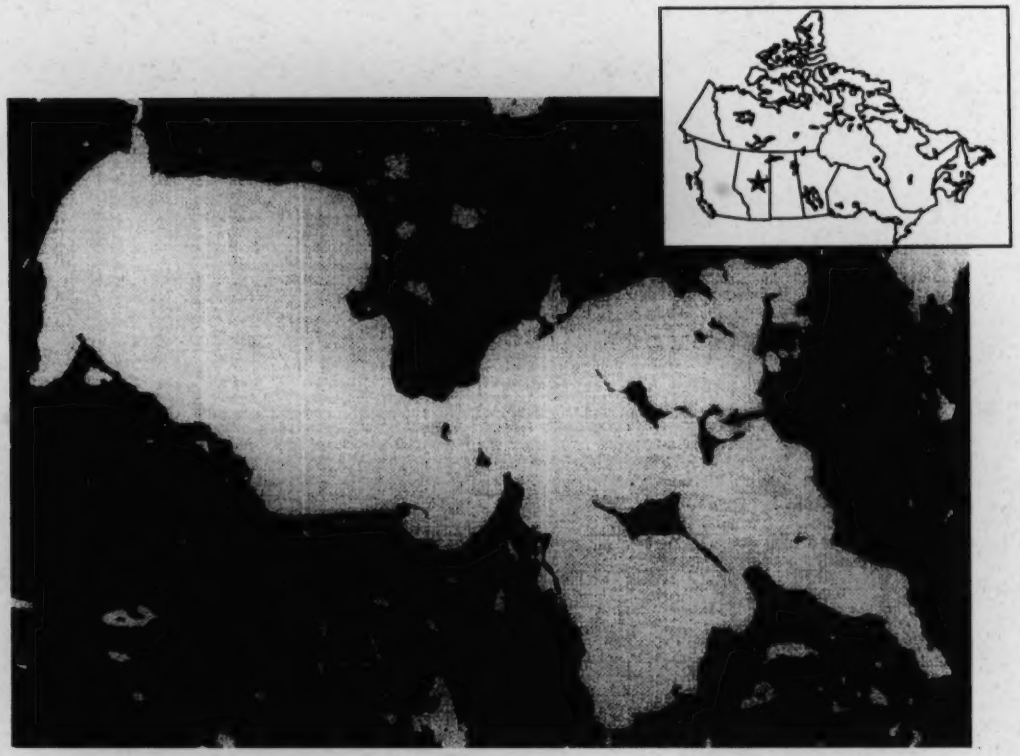

Figure 3.1. Map of Lac la Biche, Alberta. Experimental mesocosms were deployed at Currant Island as marked by the arrow. The location of the town of Lac la Biche is indicated with ✦.

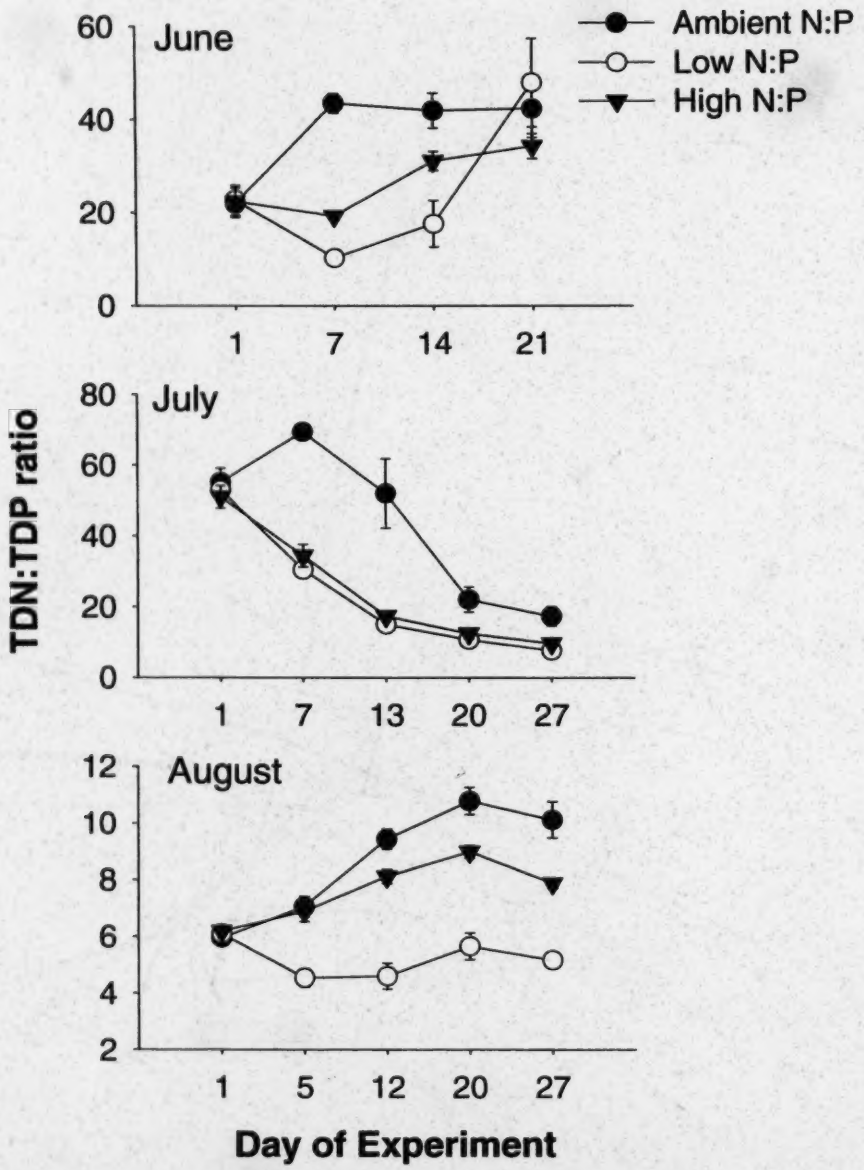

Figure 3.2. The effect of N:P treatment on TDN:TDP ratios in ambient N:P, low N:P (1.8:1) and high N:P (9:1) treated mesocosms a) June; b) July and c) August experiments. Error bars represent ±1 SE.

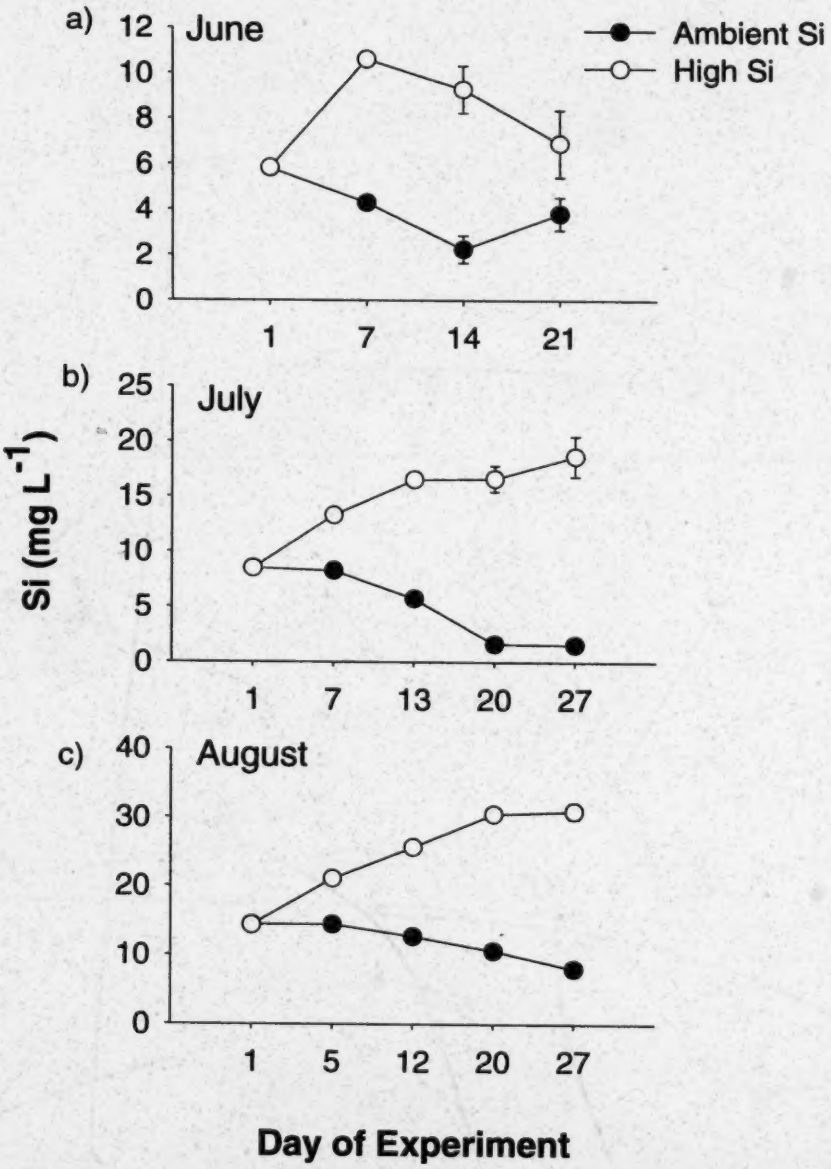

Figure 3.3. The effect of Si treatment on Si concentrations in ambient and high Si treated mesocosms in a) June; b) July and c) August experiments. Error bars represent ±1 SE.

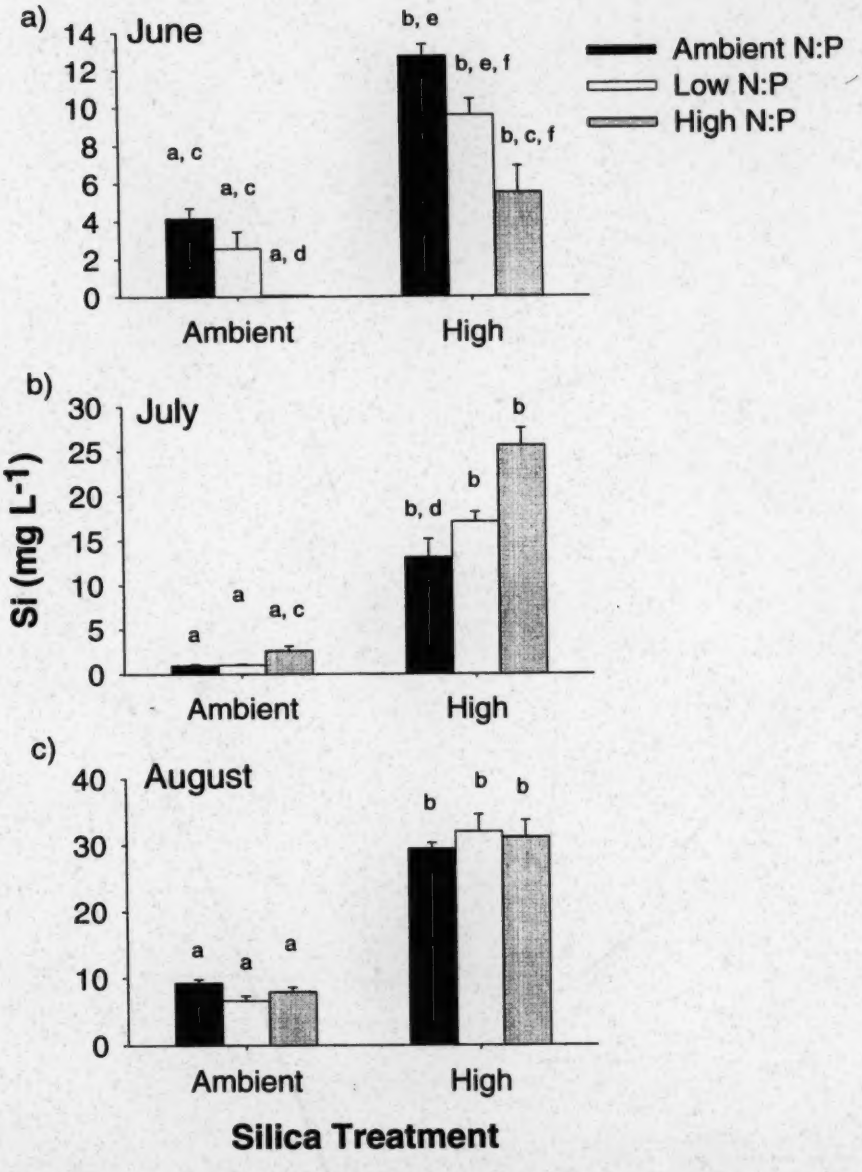

Figure 3.4. The effect of Si and N:P treatment on Si concentrations in ambient and high Si treated mesocosms. Data presented are from the day with lowest Si concentration in a) June (Day 14) b) July (Day 20) and c) August (Day 27) experiments. Error bars represent ±1 SE. Letters represent homogeneous subsets at α=0.05.

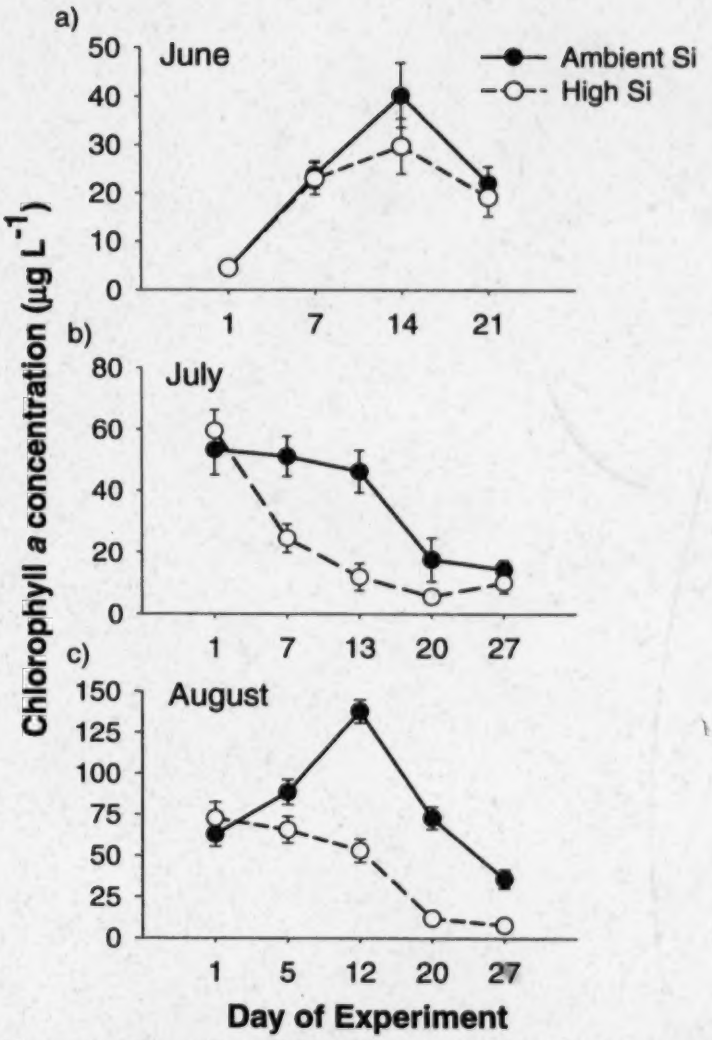

Figure 3.5. The effect of Si treatment on chlorophyll *a* concentrations in a) June b) July and c) August experiments. Error bars represent ±1 SE.

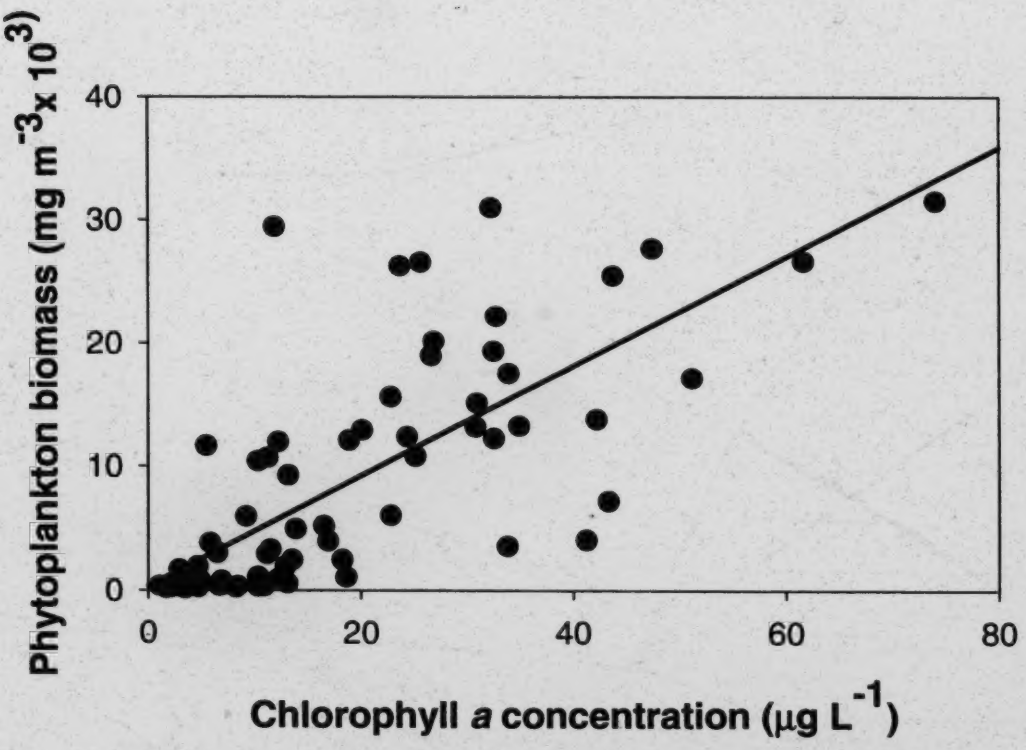

Figure 3.6. The relationship between total phytoplankton biomass and chlorophyll *a* concentration in experimental mesocosms. The variables were significantly correlated ($r=0.802$, $p < 0.001$).

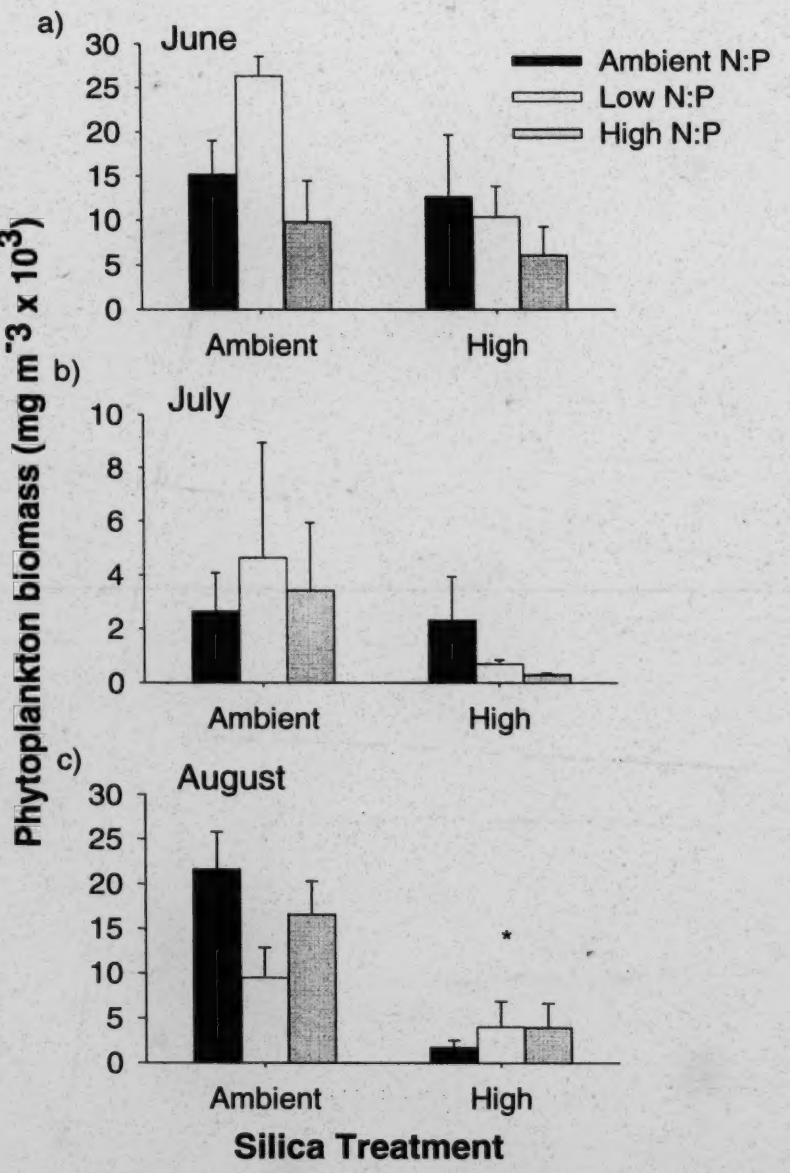

Figure 3.7. The effect of Si and N:P treatment on total phytoplankton biomass on the final day of 21-27 day experiments in a) June; b) July and c) August. Error bars represent ±1 SE. * indicates significant effect of Si treatment at $\alpha = 0.05$.

June

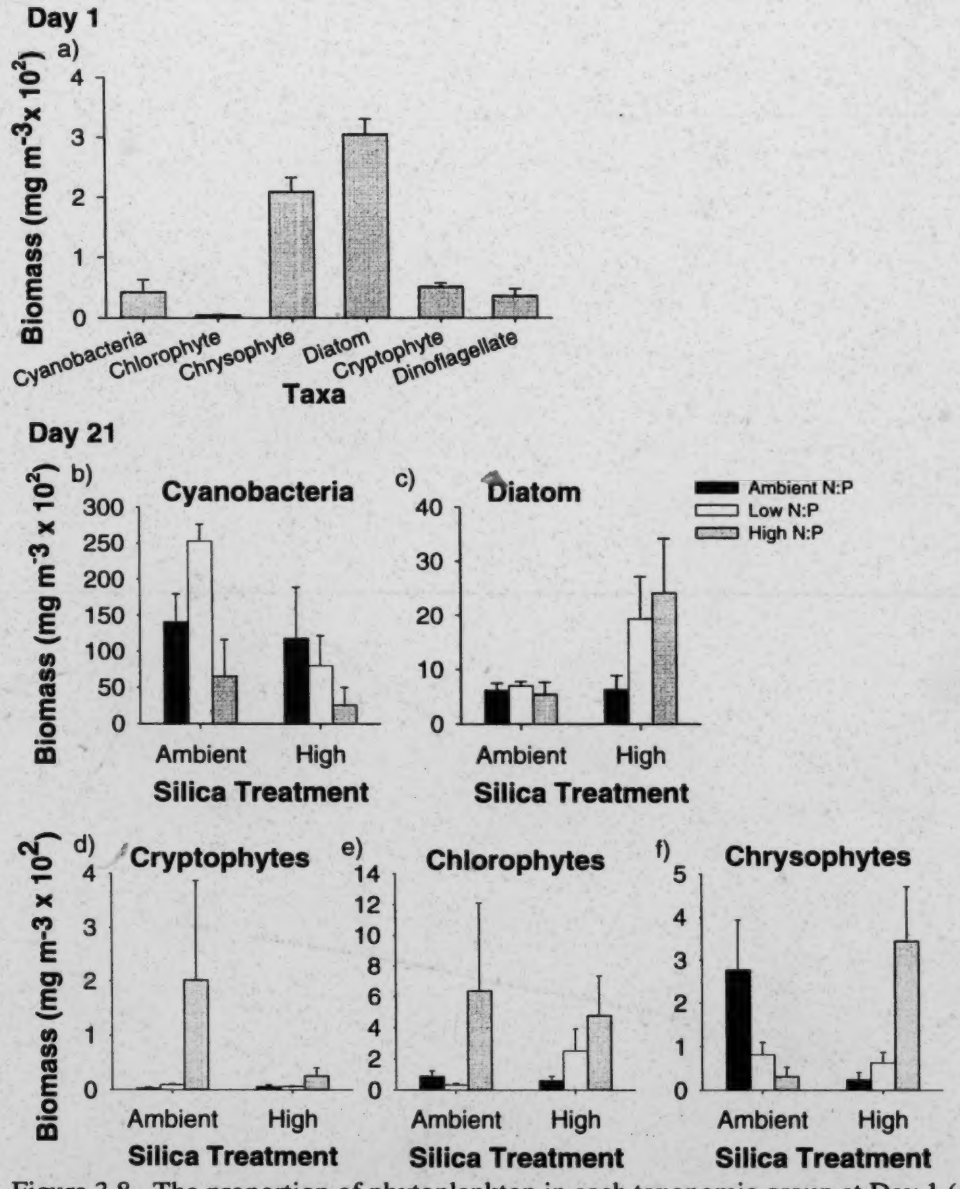

Figure 3.8. The proportion of phytoplankton in each taxonomic group at Day 1 (a) and Day 21 (b, c, d, e, f) in the June experiment. Figures b, c, d, e and f represent the biomass of Cyanobacteria, diatoms, cryptophytes, chlorophytes and chrysophytes respectively in response to silica and N:P amendment. Taxa represented comprise > 90% of the total phytoplankton biomass. Error bars represent ± 1SE.

July

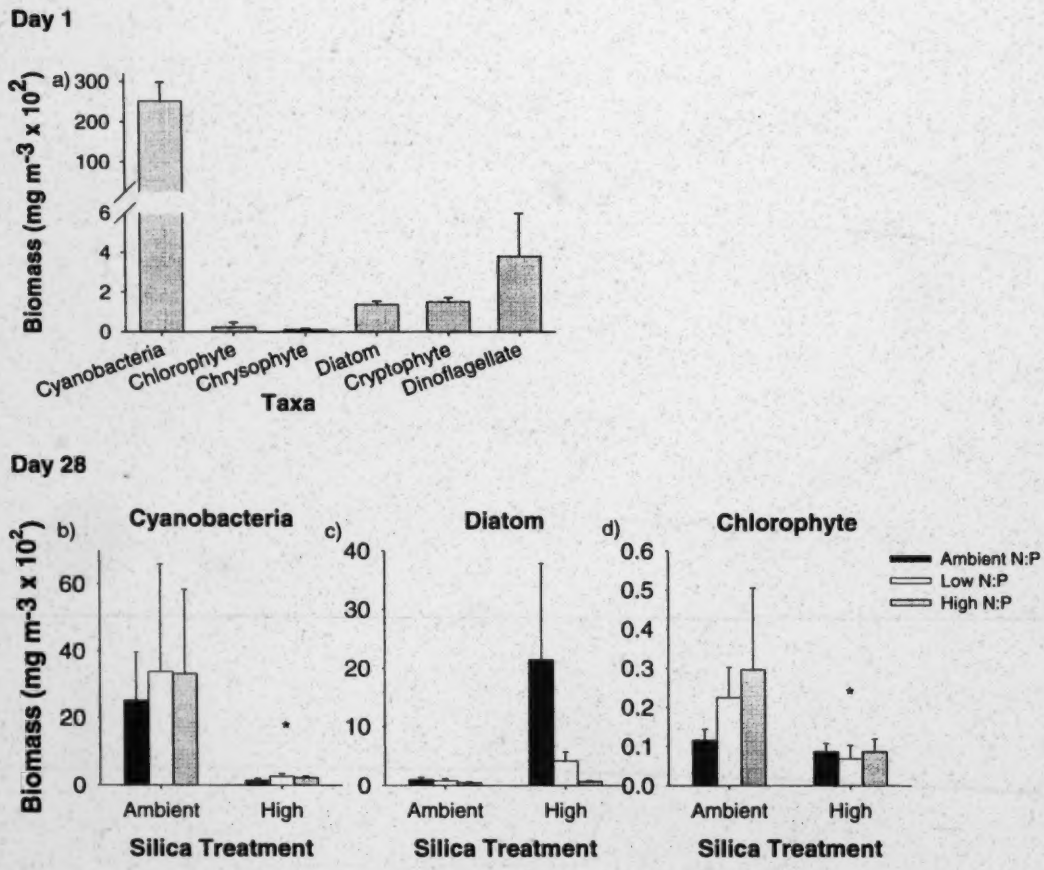

Figure 3.9. The proportion of phytoplankton in each taxonomic group at Day 1 (a) and Day 27 (b, c, d) in the July experiment. Figures b, c, and d represent the biomass of Cyanobacteria, diatoms and chlorophytes respectively in response to silica and N:P amendment. Taxa represented comprise > 90% of the total phytoplankton biomass. Error bars represent ± 1SE. * indicates significant effect of Si treatment at α=0.05.

August

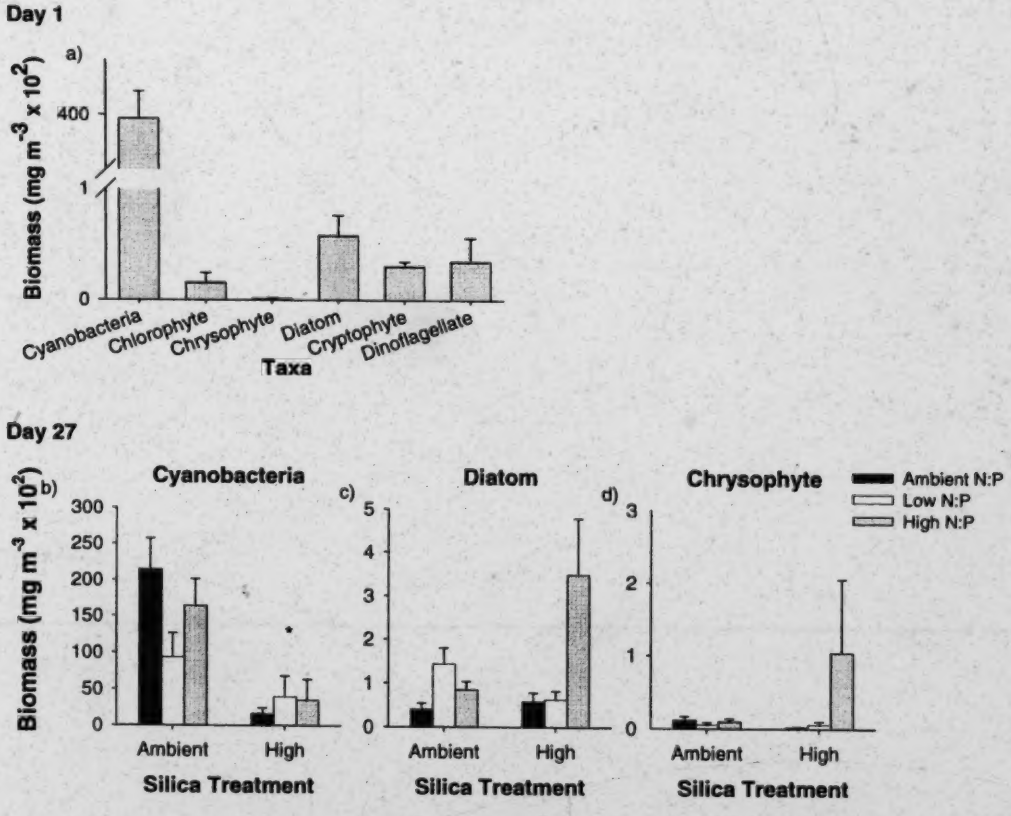

Figure 3.10. The proportion of phytoplankton in each taxonomic group at Day 1 (a) and Day 27 (b, c, d) in the August experiment. Figures b, c, and d represent the biomass of Cyanobacteria, diatoms and chrysophytes respectively in response to silica and N:P amendment. Taxa represented comprise > 90% of the total phytoplankton biomass. Error bars represent ± 1SE. * indicates significant effect of Si treatment at α=0.05.

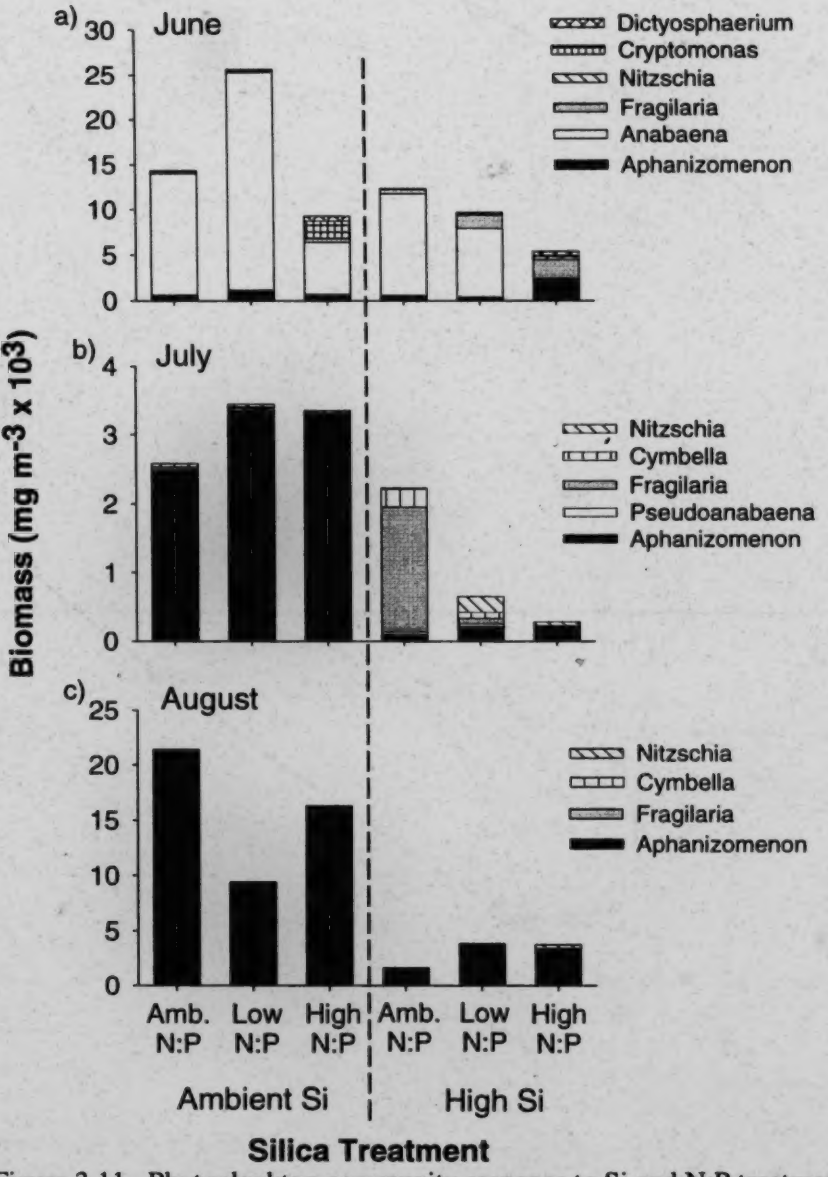

Figure 3.11. Phytoplankton community response to Si and N:P treatment on the final day of the experiment in a) June; b) July; and c) August experiments.

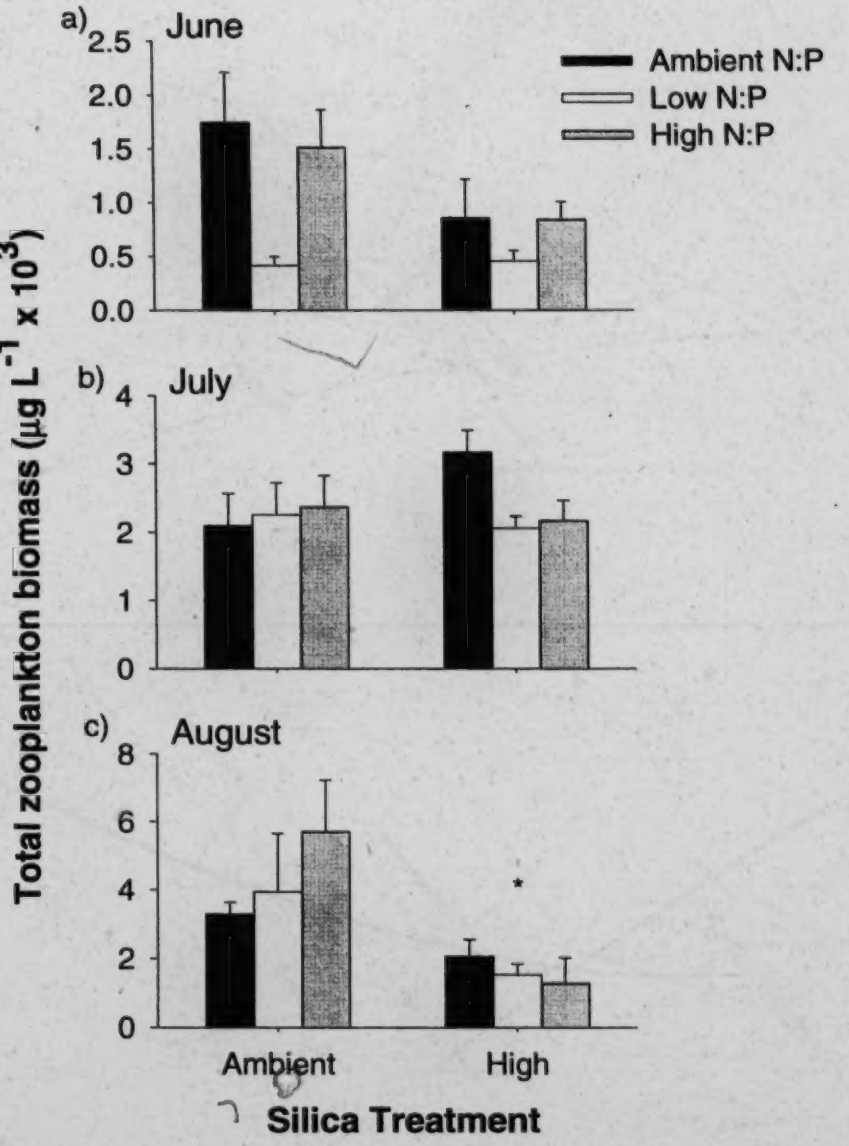

Figure 3.12. The effect of Si and N:P treatment on total zooplankton biomass on the final day of a) June; b) July and c) August experiments. Error bars represent ±1 SE. * indicates significant effect of Si treatment at α=0.05.

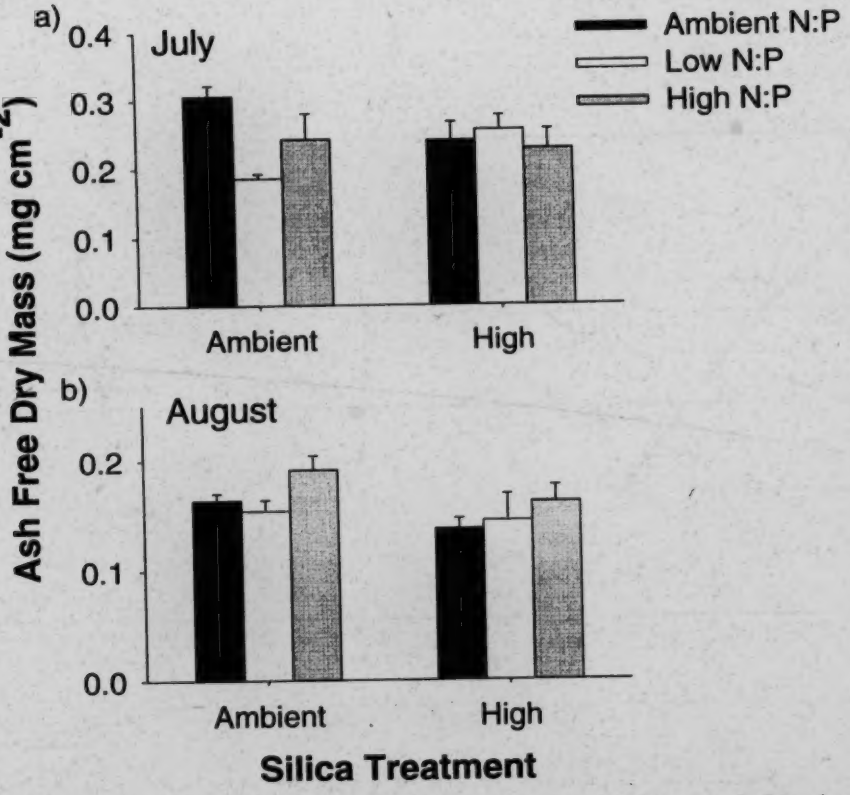

Figure 3.13. The effect of Si and N:P treatment on periphyton ash free dry mass on the final day of a) July and b) August experiments. Error bars represent ±1 SE.

Chapter 4: Conclusion

Consistent with previous research, paleolimnological analysis of sediment cores collected from Lac la Biche indicates that the lake was historically productive (Mitchell and Prepas 1990). However, loading of nitrogen (N) and phosphorus (P), total algal productivity and the abundance of Cyanobacteria have increased since ca. 1950, indicating a general decline in water quality. Despite evidence of ongoing eutrophication, increasing deposition of biogenic silica (BSi) to the sediments and increasing abundance of Cyanobacteria, I found no indication of an historical onset of silica (Si) depletion or a relative shift in the phytoplankton community to include increasing proportions of diatoms and decreasing proportions of Cyanobacteria. Thus it does not appear that Si depletion has influenced a succession of diatoms to Cyanobacteria in Lac la Biche.

As has been reported in oligotrophic lakes (Schelske et al. 1986, Schelske 1999) and in marine experiments (Doering et al. 1989, Egge and Aksnes 1992, Wassmann et al. 1996, Svensen 2002), I have shown through nutrient amendment experiments that BMSD can occur, at least on a seasonal basis, in mesocosms in a northern, hypereutrophic lake. I additionally found that the diatom community most efficiently utilized Si, thereby reduced Si concentrations to near potentially limiting concentrations, at high TDN:TDP ratios and in the early to mid- summer. Similar to previous research, Si amendment also caused significant changes to the phytoplankton community, increasing the proportion of diatoms relative to other taxa (Doering et al. 1989, Egge and Aksnes 1992, Wassman et al. 1996). Consistent with Egge and Aksnes (1992), Lac la Biche diatoms supplemented with Si recovered seasonally to dominate the phytoplankton assemblage although they formed less than 5% of the initial total phytoplankton biomass.

Based on Si concentration data collected from surveys between 2003 and 2005, Si depletion events occur only occasionally in Lac la Biche (Schindler et al., unpublished data). Under current levels of N, P and Si loading, it seems unlikely that declining Si concentrations will play an important role in the structuring of the phytoplankton community in Lac la Biche in the near future. However, Si depletion to

below potentially limiting concentrations as was seen in Lac la Biche in 2003 coincided with the highest P loading of the three years of survey data (Schindler et al., unpublished data). Additionally, Schelske (1999) found that the frequency and duration of Si depletion was proportional to the degree of eutrophication in the Laurentian Great Lakes. Therefore, with increased nutrient loading, Si depletion may become a more consistent feature in Lac la Biche.

Additionally, long term Si decline may also be caused by a reduction in Si loading (Conley and Malone 1992, Humborg et al. 2000). Si supplied to lakes decreases as stream flow decreases with drought and climate warming (Schindler et al. 1996). Areas in Western Canada are anticipated to have lower surface water flow in the future due to drought, climate warming and human induced landscape modifications in this century (Schindler and Donahue 2006). Therefore, I may expect a widespread decline in Si loading to aquatic systems (Conley and Malone 1992, Schindler et al. 1996, Humborg et al. 2000). Reductions in silica loading, coupled with the effects of eutrophication and BMSD, may increase the importance of Si depletion in restructuring aquatic environments.

There are several uncertainties that remain in understanding the role of Si depletion in eutrophication. First, it is unclear if polymictic lakes such as Lac la Biche are less susceptible to Si depletion. Frequent Si renewal to the water column through mixing events would be expected to decrease the probability of long-term Si depletion. However, in eutrophic lakes, Si dissolution from sediments occurs more efficiently during the anoxic conditions of stratification (Conway et al. 1977). Future research should include an extensive investigation of internal Si loading in polymictic lakes to resolve this issue. Analysis of the Si budget in years with variable precipitation may also help to clarify the anticipated effect of lower future surface water flow on external Si loading to Lac la Biche. Finally, experiments that quantify the effect of variable quantities of N and P addition on BMSD would help to form models to predict the effect of increased nutrient loading on Si depletion. Clarification of these issues will better inform lake managers on the critical need to manage N and P loading and consequent Si depletion in aquatic systems.

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